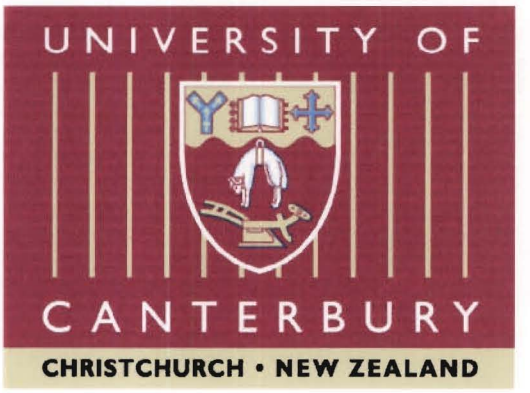
Metallosupramolecular Chemistry

A thesis submitted in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy in Chemistry
at the
University of Canterbury.

Christopher Mark Fitchett



University of Canterbury
Christchurch
New Zealand

2002

In all things of nature there is something of the marvelous.

Aristotle (384 BC - 322 BC)

If we knew what it was we were doing,
it would not be called research, would it?

Albert Einstein (1879 - 1955)

Acknowledgements

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Contents

Abstract

This thesis describes the preparation and characterisation of a number of metallosupramolecular assemblies. Such species were constructed by the reaction of ligands based on nitrogen containing heterocycles with metal atoms. The coordinate bonds used to hold these species together provide a mixture of strength and lability that aids the formation of interesting structures.

The twenty six ligands utilised for the formation of metallosupramolecular species can be divided into three types; rigid *sym*-biheterocycles, ligands with added flexibility, and chiral ligands for the formation of polymers. These investigations used a range of metal atoms to allow the examination of the metallosupramolecular chemistry of these ligands.

The structure of forty three complexes was determined using single crystal X-ray crystallography. The complexes isolated and characterised had a diverse range of structures, with discrete and polymeric species formed. The rigid *sym*-biheterocycles gave mostly monomeric and oligomeric complexes, with two polymeric complexes also formed; all ligands failed to coordinate through all donor atoms. Ligands with added flexibility gave mostly one- and two- dimensional polymers, with discrete complexes such as M_2L_2 macrocycles and mononuclear structures also formed. The chiral ligands prepared using camphor gave a range of chiral polymers, and in two cases these possessed directionality.

The variety of metallosupramolecular assemblies synthesised exemplifies the structural complexity that may be formed using metal atoms and N-heterocyclic ligands as structural components for molecular construction.

Chapter 1

Introduction

1 Introduction

Supramolecular science[1] involves the synthesis and study of molecular aggregations. These aggregations consist of molecules held together by weak non-covalent interactions, such as hydrogen bonds, π-π interactions or ionic interactions. The term supramolecular chemistry has been defined as "...chemistry beyond the molecule, bearing on the organised entities of higher complexity that results from the association of two or more chemical species held together by intermolecular forces."[2]

The synthesis of supramolecular species utilises a range of interactions that are weaker than those used in traditional chemistry. The large number of such interactions required during the preparation of a supramolecular assembly relies on the simultaneous formation of many bonds during the reaction. This is in stark contrast to the largely stepwise formation of smaller molecular species using the methodologies of traditional inorganic and organic chemistry. The simultaneous formation of many bonds facilitates the formation of large supramolecular aggregations by avoiding the loss of material due to stepwise bond forming processes and time-consuming purification procedures.

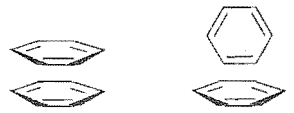
The conscious design of components that will arrange in a premeditated way to give a product with known properties remains the ultimate goal, and current research is being undertaken with this in mind. The formation of a desired architecture entails the judicious choice of starting materials which will react in a predictable way. This, therefore, requires knowledge of the properties of the building blocks and how they interact. The convergent organisation of the component species into a supramolecular object is termed *self-assembly*.

The use of weak interactions, rather than covalent bonds, allows the formation of the desired product through *thermodynamic* control. During a reaction the building blocks react to give a large number of different intermediate products. Due to the lability of the interactions between the building blocks, these intermediate products are in equilibrium with the starting materials. Therefore, continuous shuffling of possible products will, given enough time, form the most thermodynamically stable product. None of the *kinetic* products will be observed after completion of the reaction. This process of error checking allows the formation of the desired thermodynamic product often in remarkably high yield.[3]

In order to obtain the desired products it is necessary to ensure that the building blocks have the correct interaction points prior to reaction. The reactants may then simply be

added together in the appropriate ratio to generate the desired product. This 'synthon' approach requires knowledge of the types of interactions that can be used to best achieve the desired product, and the ability to introduce interacting groups into the appropriate places on the building blocks. The archetypal interaction used to form supramolecular assemblies is the hydrogen bond. Hydrogen bonding interactions occur between hydrogen atoms (donor atoms) and electronegative atoms (acceptor atoms) and are relatively weak, being of the order 5 – 30 $kJmol^{-1}$ and usually directional.[4,5] Structural arrangements which allow the formation of hydrogen bonds between molecules are common in biology, and are easily introduced into organic molecules. The formation of discrete assemblies and polymeric arrays utilising hydrogen bonding interactions has proven successful.[6]

Other interactions have been of less importance, but have proven useful for the preparation of certain supramolecular entities. Interactions between aromatic molecules have been utilised. However, these are rarely used as the only form of intermolecular attraction. They are weaker then hydrogen bonds and less directional, falling into two groups, the face-to-face interaction and edge-to-face interaction,[7,8] as shown in figure 1.1. The utility of π-π stacking in crystal structures can be observed in an analysis of the Cambridge Structural Database conducted by Janiak, which shows numerous examples of both face-to-face and edge-to-face interactions.[9]



(a) (b)

Figure 1.1 Possible π-π stacking interactions between aromatic rings. **(a)** Face-to-face, and **(b)** edge-to-face.

The formation of supramolecular species from combinations of organic molecules and metal atoms has been designated as *metallosupramolecular* chemistry, a term introduced by Constable.[10] Over the last 15 years a vast number of metallosupramolecular aggregations have been investigated. The self-assembly of metallosupramolecular assemblies from simple starting materials allows the formation of novel and interesting structures.[11] The use of metal atoms to form a large number of different structures has recently been extensively reviewed. The large number of different topologies found includes macrocyclic polygons and polyhedra,[12] helicates,[13] interlocked rings (catenanes and knots),[14] coordination polymers and networks.[15-18]

The use of the metal-ligand bond for the construction of supramolecular entities has a number of advantages over other interactions. The large number of different metals available with different properties allows the choice of a particular metal atom to suit an application. The metal-ligand bond strength can be varied, depending on the metal ion chosen, from about the strength of a hydrogen bond to that of a covalent bond. The choice of an intermediate strength interaction allows the use of fewer intermolecular interactions between the components of an assembly, while still maintaining thermodynamic stability. Metal atoms possess different properties to purely organic atoms and, when introduced into supramolecular assemblies, allow the products to have interesting functional properties. Recent investigations of the photochemistry[19] and electrochemistry[20] of large metal containing structures provides a taste of the properties available to metallosupramolecular assemblies.

The transition metal ions used for the preparation of metallosupramolecular assemblies have preferred coordination numbers and coordination geometries. The geometries available, some of which are shown in figure 1.2, often differ greatly from those available to atoms used in the preparation of purely organic supramolecules. The particular geometries available to a metal ion depend on the number and arrangement of the d-electrons. The choice of metal atom, therefore, can have a large effect on the structure of a metallosupramolecular assembly. The use of labile d^{10}-metals, which have no electronic preference for a particular coordination number or geometry, allows the formation of varied structures from the same starting materials. The complexes formed from the divalent cations of zinc and cadmium exemplify this. The smaller zinc cation prefers tetrahedral or octahedral coordination geometries, while the larger cadmium cation prefers octahedral or pentagonal bipyramidal geometries.[21]

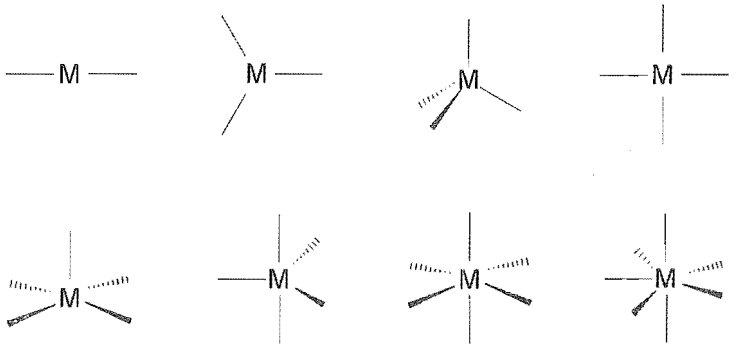


Figure 1.2 Some of the possible coordination geometries formed by metal atoms in metallosupramolecular assemblies.

The monovalent d^{10}-metal ions copper(I) and silver have proven perhaps the most popular for the formation of metallosupramolecular assemblies.[22] These labile ions form complexes with variable coordination numbers and geometries, with copper(I) most often tetrahedral. Silver can form with coordination numbers ranging between 2 and 9 and have various coordination geometries. However, the lower coordination numbers are preferred with linear and various three coordinate geometries the most common. Metal ions with other arrangements of d-electrons have more stringent preferences for coordination number and geometry. The d^9-metal copper(II) usually forms trigonal bipyrimidal or square pyramidal geometries. The divalent d^8-metal palladium ions have a strong preference for the formation of square planar coordination geometries.

The choice of metal ion must also take into account the anions and ancillary ligands coordinated, as these can have a large effect on the precise mode of coordination. While noncoordinating anions allow the maximum interaction between the ligands and the metal ions, smaller bridging anions can increase structural complexity. The use of the halides of copper(I) and copper(II) allows the assembly of oligomeric and polymeric species, with the metal centres bridged by halide ions. The formation of complex polymeric structures from copper(I) halides, particularly iodide, allows interesting mixed inorganic and coordination compounds.[23] Copper(I) iodides give a large variety of interesting structures, some of which are shown in figure 1.3.[24] Interestingly, tetranuclear cube-like copper(I) iodide complexes have been recognised as having useful luminescent properties.[25]

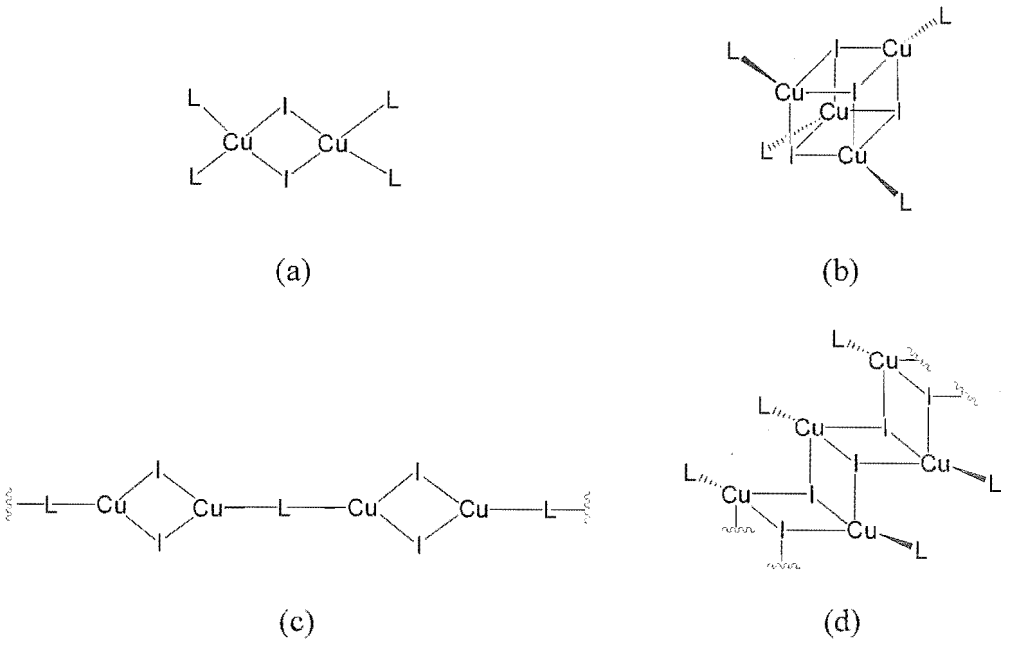
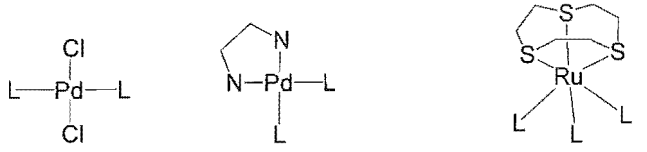


Figure 1.3 Some of the topologies formed by copper(I) iodide involving bridging iodine atoms, **(a)** dinuclear, **(b)** tetranuclear cube, **(c)** polymer of dinuclear units and **(d)** staircase chain.

Other metal ions with coordinated anions and ancillary ligands allow the restriction of coordination geometries. Palladium chloride, with *trans*-coordinated chloride anions, allows the formation of linear bridges, while palladium with a *cis*-coordinated ligand, such as ethylenediamine, forms a 90° bridge. These examples are shown in figure 1.4(a). More complicated geometries may be formed with appropriately substituted metal atoms. A facially capped octahedral metal atom, such as ruthenium, provides three mutually orthogonal donor sites, as shown in figure 1.4(b). These metal fragments have all been used to form discrete cyclic complexes, such as squares,[26] cubes,[27] and cage-like structures.[28]



(a) (b)

Figure 1.4 Examples of metal ions with coordinated anions and ancillary ligands, with **(a)** palladium as a linear and 90° bridge and **(b)** ruthenium with a facial capping [9]aneS_3 ligand.

The ligand chosen is also an important factor in determining the structure of a supramolecular aggregation. The use of *exo*-bridging ligands, which can bridge two metal atoms, allows the formation of the large assemblies containing multiple metal atoms. Any ligands used must be able to bond to metal atoms in a semi-predictable manner, to allow the formation of the desired product. The ligands can have more structural complexity than the metal atom, as they do not rely on the chemistry of a single atom. The design of bridging ligands with multiple donor sites has become a complicated undertaking, with ligands of increasing complexity used to form metallosupramolecular arrays. A small selection of the many possible bridging modes of ligands are shown in figure 1.5.

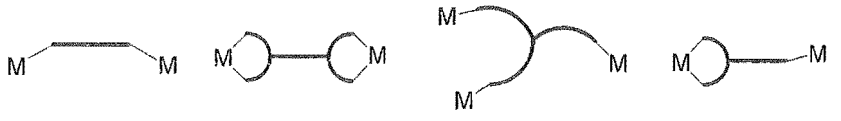


Figure 1.5

In order to maintain thermodynamic control it is necessary to use ligands with donor atoms that allow the formation of labile metal-ligand coordination bonds. Ligands constructed from nitrogen containing heterocycles have been used extensively in coordination chemistry, and their properties as part of coordination bonds make them ideal for formation of metallosupramolecular assemblies. Six membered aromatic rings containing nitrogen atoms, such as pyridine (fig 1.6(a)), have been used extensively for this purpose, as they form coordinate bonds to most of the metals in the periodic table. The chelating ligand 2,2′-bipyridine (fig 1.6(b)) is one of the most important ligands in coordination chemistry, [29] and many of its derivatives have been used as a component in supramolecular chemistry.[30] The *exo*-bridging ligands 4,4′-bipyridine (fig 1.6(c)) and pyrimidine (fig 1.6(d)) are examples of simple N-heterocyclic ligands which have been used to form metallosupramolecular arrays. The range of ligands which may be constructed from aromatic six-membered heterocyclic rings is limited only by the imagination of the chemist, as many synthetic techniques are available for their formation.

(a) (b) (c) (d)

Figure 1.6

The development of single crystal X-ray diffraction as a tool for the determination of three-dimensional structure has led to a large increase in the number of investigations of supramolecular chemistry. X-ray diffraction is unparalleled in its ability to unambiguously determine the overall structure of supramolecular assemblies in the solid state. Supramolecular arrays often fall into the intermediate ground between small molecule and protein crystallography. This means that collection of large amounts of data is often necessary for crystals involving supramolecular structures. The advent of CCD-based detector technology[31] and fast personal computers has alleviated these problems, and changed the time-span of an X-ray structure determination from weeks and months to days (and even to hours!!). However, single crystal X-ray structure determination requires, not only that the compound form single crystals, but that these crystals be of good quality. Loss of solvent, twinning, insufficient volume, and instability under X-ray bombardment can cause a data collection to be ineffective. The problem of disorder can cause more difficulty in supramolecular crystallography than small molecule crystallography due to the

large number of counterions and solvate molecules often associated with supramolecular assemblies. Despite these problems single crystal X-ray diffraction is the method of choice for three-dimensional structure determination in the majority of cases. Other techniques such as NMR spectroscopy and mass spectrometry have also been used, but three-dimensional structure determinations are less applicable to these techniques. During the course of this thesis, single crystal X-ray diffraction has been used extensively to determine three-dimensional structure.

This thesis describes the synthesis of twenty six ligands, seventeen of which have not been reported previously. All the ligands are based on six-membered heterocyclic rings, with nitrogen heteroatoms. A selection of *sym-biheterocycles*, which have previously been largely ignored, *flexible ligands* with an aromatic core, and ligands capable of forming *chiral coordination polymers* have been investigated. The coordination chemistry has been investigated with various metal ions capable of forming metallosupramolecular assemblies, concentrating particularly on labile metal atoms for the reasons outlined above. In total, 100 transition metal complexes have been prepared and characterised. Single crystal X-ray structure analysis has been used as the primary means of structure determination, and this thesis includes forty nine novel X-ray crystal structure determinations of forty three complexes and six ligands.

Chapter 2

Naphthalene based Sym-Biheterocycles

2 Naphthalene based *Sym*-Biheterocycles [§]

2.1 Introduction

The importance of simple N-biheterocyclic ligands, such as 2,2′-bipyridine (fig 2.1), in coordination and supramolecular chemistry has been outlined in chapter 1. Extensive use has been made of rigid *exo*-ligand molecules with defined geometry in metallosupramolecular chemistry. These have at least two donor atoms that can coordinate different metal atoms. Such ligands can bridge metal atoms with a predetermined geometry, and as such represent components for the construction of discrete and polymeric complexes.[33]

Simple *exo*-ligands have been used widely in the construction of various structural motifs. The combination of 4,4′-bipyridine with metal atoms that are restricted to *cis*-coordination geometries leads to the formation of discrete cyclic structures, including triangles[26] and squares.[34,35] The use of metal atoms with less defined geometries has led to the formation of a large number of polymeric complexes. The formation of 1-D,[36] 2-D,[37] and 3-D[38,39] polymers has been observed, depending on the choice of metal atom.

Figure 2.1

Ligands with multiple binding sites enable the formation of structures with greater structural diversity than is available to simple bridging or chelating ligands. The use of so-called 'multinodal' ligands formed from N-heterocyclic molecules has proven a popular approach, as such molecules have well defined geometries.[40] Heterocycles that combine chelating and bridging geometries (fig 2.2) have given rise to the formation of 1-D, 2-D and 3-D polymeric complexes with various topologies.[41]

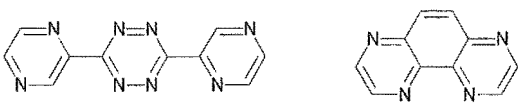


Figure 2.2

[§] For the purposes of this thesis *sym*-biheterocycles are defined as identical heterocyclic groups linked through the same ring atom via a single bond.[32]

'Multinodal' biheterocycles are a natural progression from the ligands described above. The combinations of donor atoms used allow an extension of the available binding modes. The combination of the nitrogen donor atoms of 2,2′-bipyridine and 4,4′-bipyridine can be seen in the biheterocycle 4,4′-bipyrimidine (fig 2.3), and the resulting molecule has the ability to either chelate or bridge, or, perhaps more interestingly, a combination of both. Recent investigations of the coordination complexes formed by the related biheterocycle 2,2′-dimethyl-4,4′-bipyrimidine (fig 2.3) exemplify the versatile nature of these ligands with the formation of numerous different topologies.[42,43]

Figure 2.3

Rigid *exo*-ligands which bridge at angles less than 180° have been less well investigated. The use of the 'multinodal' molecule, 2,2′-bipyrazine (fig 2.4) has shown the utility of such multidentate ligands. As a ligand, 2,2′-bipyrazine forms coordination complexes with various metals to give polymeric and discrete species.[44,45] The complexes of 2,2′-bipyrazine with M(en) (M=Pd, Pt) (fig 2.4) are precursors for the formation of complexes which allow the formation of mixed-metal complexes, with the ligand of the precursor locked in a *cisoid* conformation by the coordinated Pd or Pt atom. This has allowed the formation of triangular species, and aggregations composed of triangular subunits.[46]

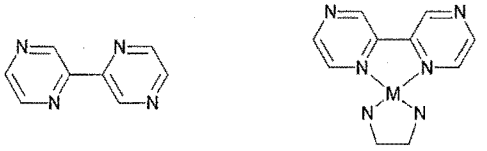


Figure 2.4

The azine and diazine-based biheterocyclic systems based on benzene, such as those outlined above, are common in coordination chemistry.[33,47] Considering the ubiquitous nature of such systems, it is rather surprising that naphthalene based biheterocycles have not achieved the same status. A possible exception is 2,2′-biquinoline and its derivatives (fig 2.5), which have found use as chelating compounds in studies of ruthenium chemistry,[48] and for quantitative analysis of copper (e.g. in protein analysis).[49] The use of such benzo-fused azines increases the steric bulk in the region of the nitrogen donor atoms, possibly explaining their lack of use in coordination chemistry. The formation of

metallosupramolecular species from binaphthalene based heterocycles remains largely unexplored.

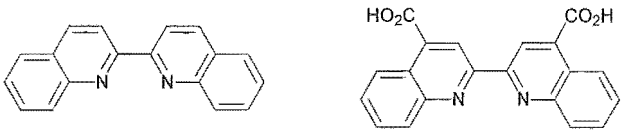
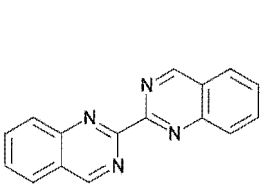
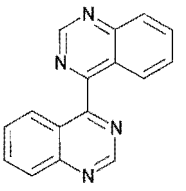


Figure 2.5

This chapter describes the preparation of complexes of the known *sym*-biheterocycles **2.1** – **2.5** (fig 2.6). Four of the molecules represent possible 'multinodal' ligands, while the remaining molecule is a potential bridging ligand; all have received little attention as ligands for coordination chemistry.



2.1



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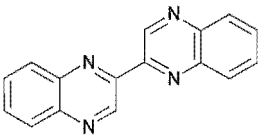

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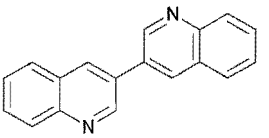

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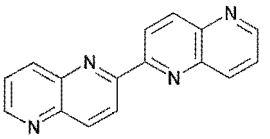
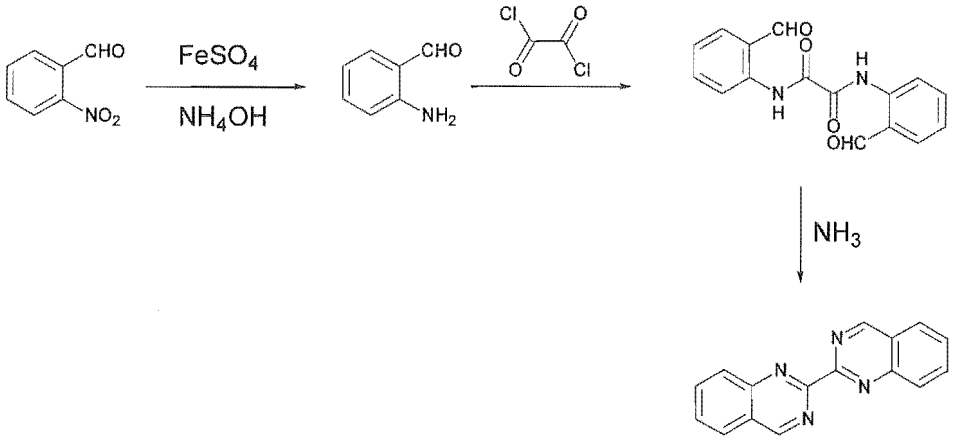


2.5

Figure 2.6

2.2 Ligand Synthesis

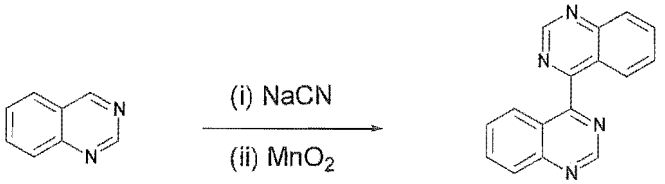
Potential ligands **2.1** – **2.4** were synthesised by literature methods. 2,2′-Biquinazoline (**2.1**) was synthesised by the ring closure of N,N′-(di-*o*-formylphenyl)oxanilide using ammonia in a sealed tube, as shown in scheme 2.1, following the method of Armarego and Willette.[50] The product, **2.1**, was isolated in good yield (78%) as yellow crystals.



2.1

Scheme 2.1

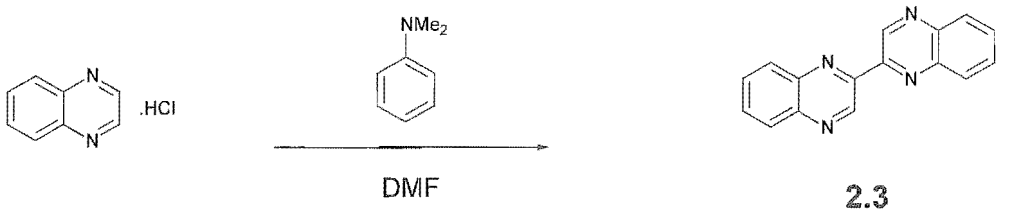
4,4′-Biquinazoline (**2.2**) was synthesised using the method of Armarego and Willette,[50] which involved the reaction of quinazoline with sodium cyanide, followed by oxidation of the intermediate with manganese dioxide, as shown in scheme 2.2. The potential ligand, **2.2**, was isolated in modest overall yield (46%) as a colourless crystalline powder.



2.2

Scheme 2.2

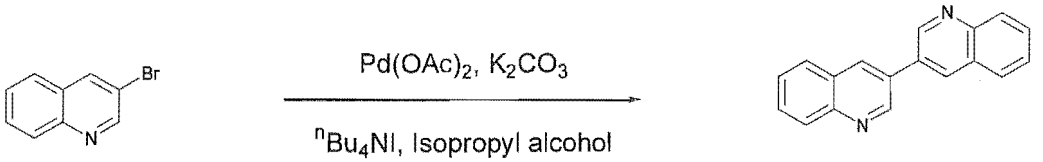
2,2′-Biquinoxaline (**2.3**) was synthesised using the method of Chupakhin et al.,[51] which involves the radical coupling of quinoxaline hydrochloride using N,N-dimethylaniline in dimethylformamide (scheme 2.3). Potential ligand **2.2** was isolated in moderate yield (61%) as a red solid.



2.3

Scheme 2.3

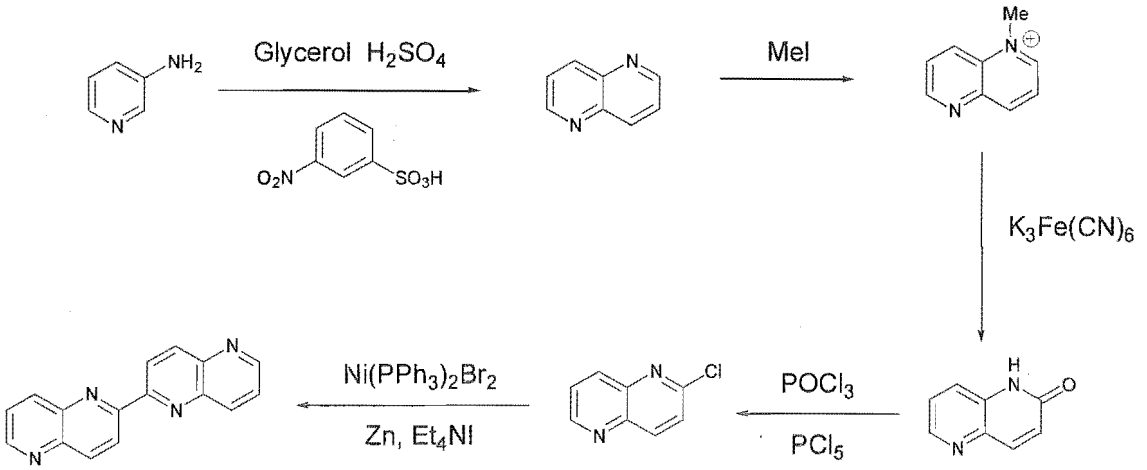
3,3′-Biquinoline (**2.4**) was synthesised by the homocoupling of 3-bromoquinoline using palladium acetate, as shown in scheme 2.4, following the procedure of Hassan et al.[52] It was obtained in modest yield (56%) as a yellow solid.



2.4

Scheme 2.4

2,2′-Bi-1,5-naphthyridine (**2.5**) has previously been synthesised by reductive coupling of 1,5-naphthyridine using palladium on carbon, although it could only be isolated in poor yield (8%).[53] Instead, **2.5** was synthesised using a Ni^0-catalysed coupling reaction, based on the methodology of Iyoda et al.,[54] as shown in scheme 2.5.



2.5

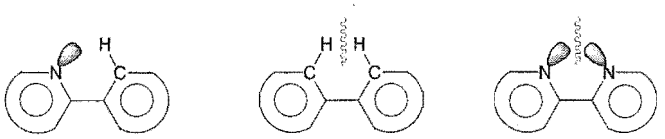
Scheme 2.5

The precursor 2-chloro-1,5-naphthyridine was synthesised by chlorination of 1-methyl-1,5-naphthyridine(1H)-2-one[55] using phosphorus pentachloride in refluxing

phosphorus oxychloride. The potential ligand **2.5** was isolated from the coupling reaction in 22% yield as a yellow solid.

2.3 Crystal Structures of Ligands

The study of the conformations of biheterocycles has been an area of much recent interest.[32] It has been proposed that the conformation is determined by through space interactions between the two ring systems.[56] Attractive interactions, based on intramolecular hydrogen-bonding (fig 2.7(a)), and repulsive interactions, involving steric interactions (fig 2.7(b)) and electrostatic interactions (fig 2.7(c)), establish the conformation of the biheterocycle. Attractive interactions promote coplanarity of the heterocycles, which is also favoured by conjugation effects, while repulsive interactions disfavour coplanarity. This proposal is supported by considerable evidence from gas-phase, solution and computational studies.[32] The biheterocycles produced in this study represent examples which incorporate the interactions used to rationalise the conformations of such compounds. Thus, it was decided to obtain single crystal X-ray structures of **2.1** – **2.4** to determine their conformations in the solid state.



(a) (b) (c)

Figure 2.7 Through space interactions of biheterocycles.

Crystals of **2.2** and **2.4** suitable for single crystal X-ray structure analysis were obtained from the slow evaporation of acetonitrile and methanol solutions of **2.2** and **2.4**, respectively. Good quality crystals of **2.1** were obtained directly from the reaction mixture, while crystals of **2.3** were obtained by layering methanol onto a dichloromethane solution of **2.3**.

Ligands **2.1**, **2.3** and **2.4** all crystallize in the monoclinic space group $P2_1/n$, each with half the molecule in the asymmetric unit. The structures of **2.1**, **2.3** and **2.4**, shown in figures 2.8, 2.9 and 2.10, respectively, are planar, with mean deviations from planarity of 0.022(4)Å, 0.019(3)Å and 0.022(5)Å, respectively. The two halves of each molecule are related through a centre of symmetry at the mid-point of the inter-heterocycle bond, which means all are in a *trans*-coplanar conformation in the solid state. The structures of **2.1** and

2.4 are in this conformation despite having two pairs of repulsive N:···:N or C-H···H-C interactions.

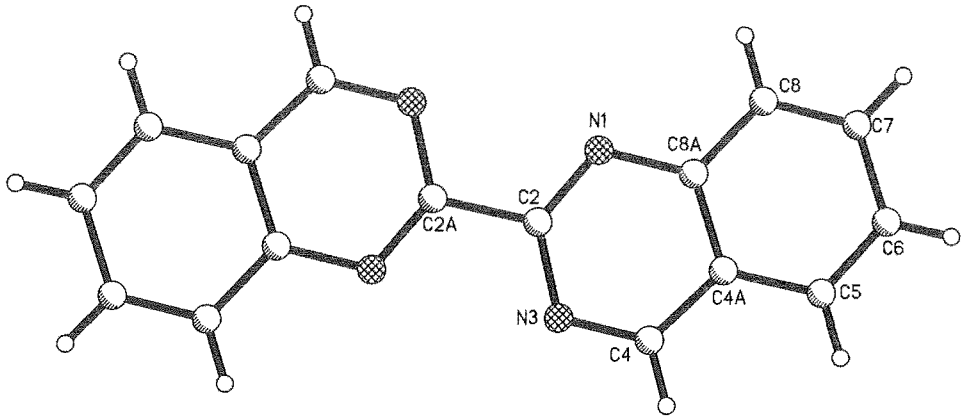


Figure 2.8 Perspective view of **2.1**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1-C2 1.318(3), N1-C8A 1.371(3), C2-N3 1.379(2), C2-C2A 1.507(4), N3-C4 1.312(3), C2-N1-C8A 116.291(7), N1-C2-N3 127.2(2), N1-C2-C2A 117.4(2), N3-C2-C2A 115.4(2), C4-N3-C2 116.4(2), N3-C4-C4A 122.8(2), N1-C8A-C4A 121.3(2).

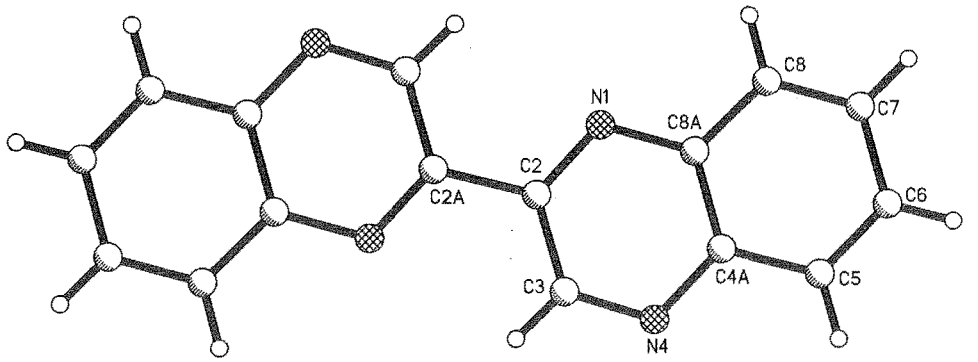


Figure 2.9 Perspective view of **2.3**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1-C2 1.318(1), N1-C8A 1.370(1), C2-C3 1.4211(15), C2-C2A 1.478(2), C3-N4 1.313(1), N4-C4A 1.368(1), C2-N1-C8A116.6(1), N1-C2-C3 121.6(1), N1-C2-C2A 118.1(1), C3-C2-C2A 120.3(1), N4-C3-C2 123.5(1), C3-N4-C4A 115.96(9), N4-C4A-C5 119.5(1), N4-C4A-C8A 121.1(1), N1-C8A-C8 119.7(1), N1-C8A-C4A 121.20(9).

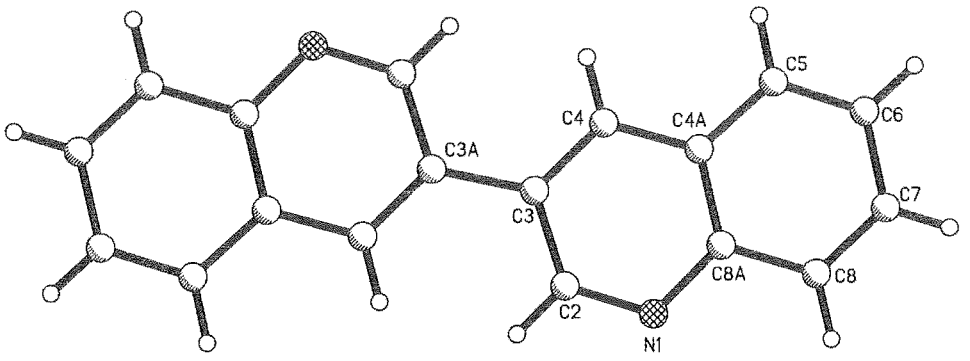


Figure 2.10 Perspective view of **2.4**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1-C2 1.303(3), N1-C8A 1.355(3), C2-C3 1.405(3), C3-C4 1.351(3), C3-C3A 1.473(4), C4-C4A 1.391(3), C2-N1-C8A 117.1(2), N1-C2-C3 125.3(2), C4-C3-C2 116.6(2), C4-C3-C3A 123.5(3), C2-C3-C3A 119.8(3), C3-C4-C4A 120.3(2), N1-C8A-C4A 122.1(2), N1-C8A-C8 118.1(2).

Packing forces are significant in the solid state. In aromatic molecules such interactions are dominated by those that involve the π-ring system;[9] π-π stacking, edge-to-face interactions and conjugation effects favour planar structures for molecules with conformational freedom. The packing of **2.1**, **2.3** and **2.4** is of the so-called γ-herringbone type,[57] with the planar heterocyclic molecules stacked along the *b*-axis of the unit cell. The packing structure of **2.4** is shown in figure 2.11 as an example of this type of packing.

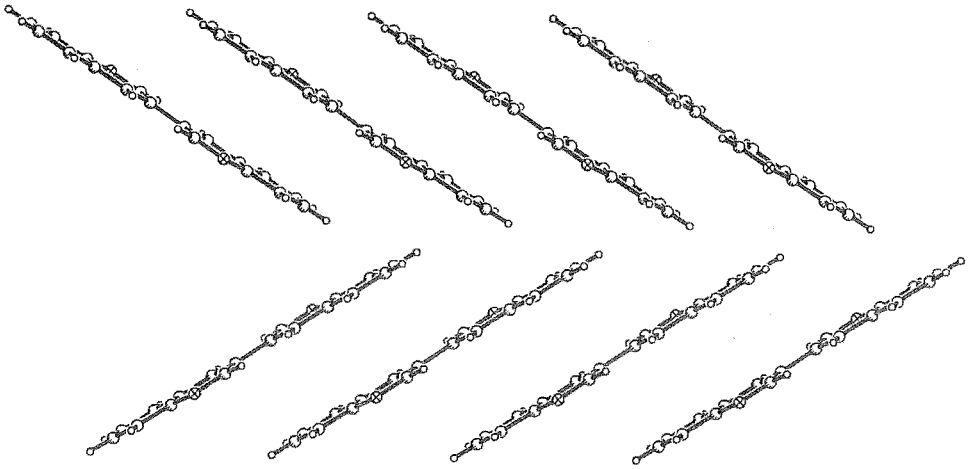


Figure 2.11 View of the packing of **2.4**, showing π-π stacking and edge-to-face interactions.

The molecules arrange with each quinoline ring stacked on top of another, but offset, so that the linking carbon atom lies over the centre of an adjacent benzo-ring. It has been proposed that such offset stacks maximise the electrostatic attraction between coplanar aromatic systems.[8] The distances between the coplanar rings in the structures of **2.1**, **2.3** and **2.4** are 3.410(4)Å, 3.428(3)Å and 3.398(5)Å, respectively, which are similar to the distance between the planes of carbon atoms in graphite (3.35Å). The γ-herringbone pattern also allows edge-to-face interactions to occur between molecules of different stacks. The closest distances between the edge of one stack and the rings of the adjacent stack for **2.3** and **2.4** occurs between H7 or H6 and the ring-plane and are 2.71(5)Å and 2.69(5)Å, respectively. The closest distance for **2.1** occurs between H6 and the ring plane and is 2.87(5)Å, and this difference represents a slight rotation of molecules of **2.1** in the stacks. These distances are typical for such interactions.[7] The angle between the molecules of different stacks varies from 64° in the structures of **2.1** and **2.4**, to 80° for the structure of **2.3**.

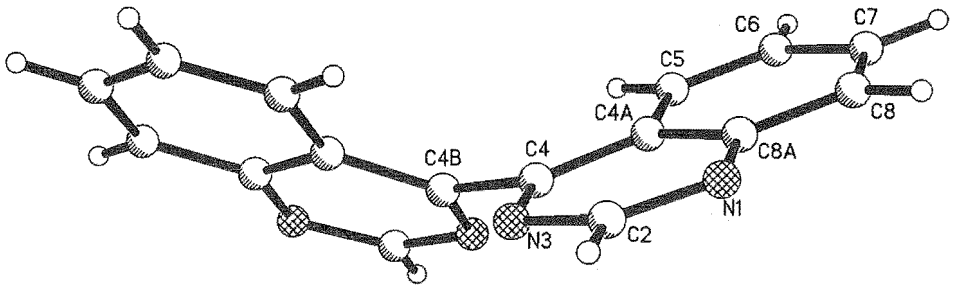


Figure 2.12 Perspective view of **2.2**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1-C2 1.318(3), N1-C8A 1.375(3), C2-N3 1.364(3), N3-C4 1.324(3), C4-C4A 1.440(3), C4-C4B 1.496(5), C2-N1-C8A 116.0(2), N1-C2-N3 127.7(2), C4-N3-C2 117.2(2), N3-C4-C4A 121.6(2), N3-C4-C4B 116.3(2), C4A-C4-C4B 122.1(2), N1-C8A-C4A 121.6(2).

Ligand **2.2** crystallizes in the monoclinic space group C2, with half the molecule in the asymmetric unit. The structure of **2.2**, shown in figure 2.12, is non-planar, with an angle of 50.9(1)° between the meanplanes of the quinazoline rings. The molecule forms this way despite a possible C-H···N interaction between H5 and N3′, which should favour planarity. The molecules stack along the *b*-axis of the unit cell, as shown in figure 2.13, with the

rings 3.531(5)Å apart, indicating a weaker π-π stacking interaction than for **2.1**, **2.3** or **2.4**. There is no indication of any H-bonding or edge-to-face interactions between the stacks of molecules.

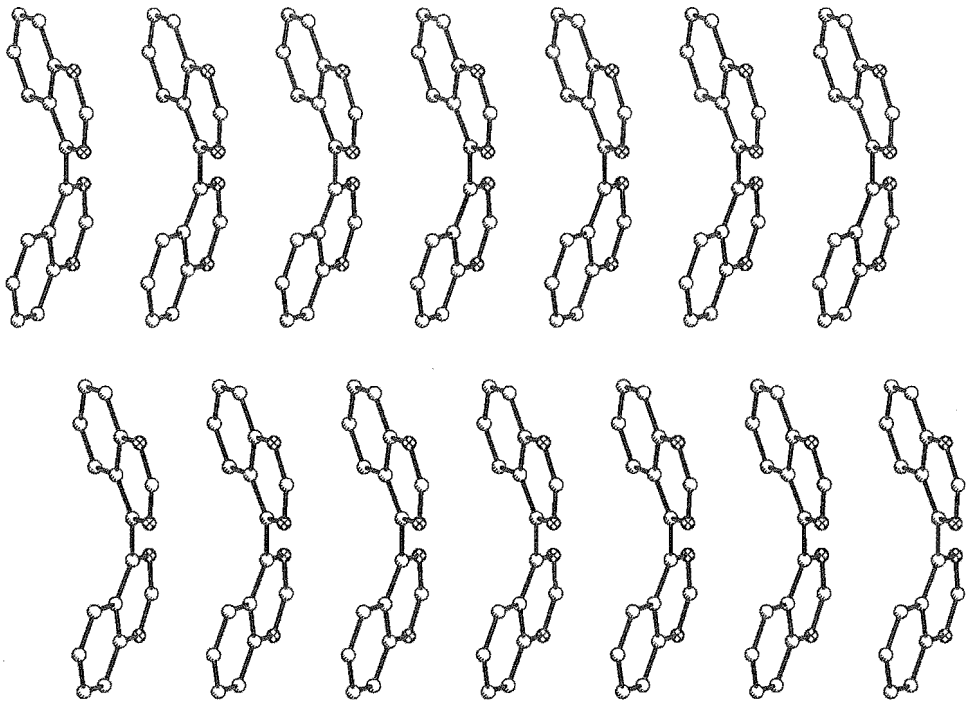
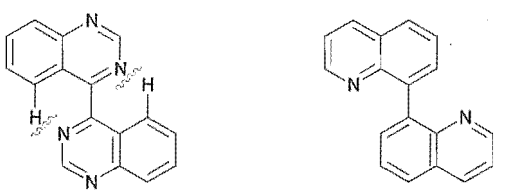


Figure 2.13 View of the packing of **2.2** along the *b*-axis.

It is possible that **2.2** is not in a *trans*-conformation due to the increased steric strain of this arrangement, shown in figure 2.14(a). 8,8′-Biquinoline (fig 2.14(b)) is a biheterocycle similar to **2.2**, as it has a 6-membered aromatic ring fused adjacent to the ring junction. A possible intramolecular hydrogen bond exists between N1 and H7′, and this structure corresponds to the transposition of N2 and H8′ in **2.2**. The structure of 8,8′-biquinoline is also non-planar, with the quinoline rings at an angle of 98.6°.[58]



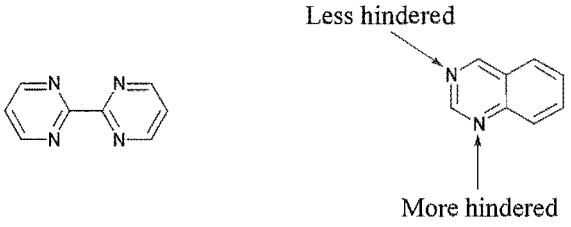
(a) (b)

Figure 2.14 **(a)** Steric strain in **2.2**, **(b)** 8,8′-biquinoline.

These results lead us to contest the proposal that the conformations of such molecules are determined by inter-ring interactions. Instead, we believe that in the solid state such molecules will always be planar unless there is a benzo-ring fused adjacent to the inter-ring bond. Planarity maximises conjugation, minimises dipole moments and allows optimal face-to-face and edge-to-face intermolecular stacking.

2.4 2,2′-Biquinazoline

The chemistry of chelating bridging biheterocycles is well studied, with 2,2′-bipyrimidine, shown in figure 2.15(a), possibly the most utilized example. Numerous hetero- and homo-dinuclear complexes, as well as mononuclear complexes of 2,2′-bipyrimidine have been studied. The fusion of benzo-rings to the *d*-bond of the pyrimidine ring differentiates the nitrogen atoms into 'less hindered' and 'more hindered', as shown in figure 2.15(b).



(a) (b)

Figure 2.15 **(a)** 2,2′-Bipyrimidine, **(b)** quinazoline ring showing the 'less hindered' and 'more hindered' nitrogen atoms.

2,2′-Biquinazoline (**2.1**) was first prepared 37 years ago.[50] The formation of mononuclear and binuclear complexes of Hg, Pd, Pt, Ru, Mo and Cu(I) with **2.1** has been investigated by Honey.[59] Some mixed-metal complexes were also synthesised using Ru and Pd. These complexes were partially characterised using mass spectroscopy, elemental analysis, and NMR.

The ligand, **2.1**, can form mononuclear chelating complexes with metal atoms in three ways, depending on the position of the fused benzo-ring. The possibilities, shown in figure 2.16, are (a) through the least hindered nitrogen atoms, (b) through the most hindered nitrogen atoms or (c) a mixture of the two. It was shown by Honey that **2.1** forms mononuclear complexes both through the least hindered nitrogens (fig 2.16(a)), and through a mixture of the most and least hindered nitrogens (fig 2.16(c)). To investigate

further the coordination chemistry of **2.1**, it was decided to make complexes using metals that were untried by Honey.

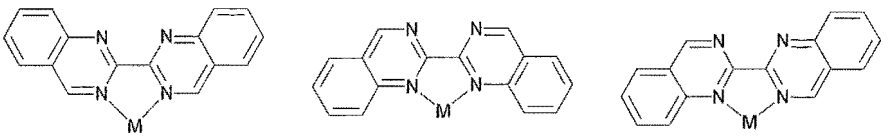


Figure 2.16 Possible mononuclear chelating complexes of **2.1**.

2.4.1 Coordination chemistry of 2.1

Complexes of **2.1** were prepared using $AgNO_3$ (**2.6**), $PdCl_2$ (**2.7**), $CuCl_2$ (**2.8**), CuI (**2.9**) and $Cd(NO_3)_2$ (**2.10**). The reaction of **2.1** with silver nitrate produced a grey solid, which analysed as $[(AgNO_3)_2.(\mathbf{2.1})]$. Despite numerous attempts to grow crystals of this complex, none were formed. The complex was soluble in donating solvents, such as acetonitrile, and an NMR spectrum showed only free ligand.

The palladium complex, **2.7**, was soluble in donating solvents, such as DMSO, and an NMR spectrum showed this to be the same as that isolated by Honey. To determine if his structural assignment was correct, crystals were grown by immersion of a dichloromethane solution of **2.1** inside a solution of Li_2PdCl_4 in methanol, as shown in fig 2.17.

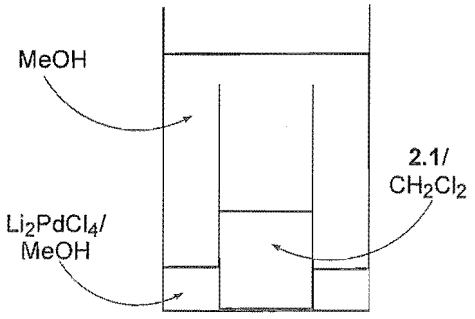


Figure 2.17 Immersion method for growing crystals of **2.7**.

The copper(II) chloride complex, **2.8**, was found to have a 1:1 metal to ligand stoichiometry and was soluble in DMF, which could indicate a monomeric or oligomeric complex. To determine the structure crystals suitable for X-ray diffraction were grown by

diffusion of acetonitrile into a DMF solution of **2.8**; these crystals analysed as [$CuCl_2$.(**2.1**).½DMF].

The copper(I) iodide complex, **2.9**, was isolated as a black solid. This analysed as [Cu_2I_2.(**2.1**)] and was extremely insoluble, possibly indicating a polymeric structure. No further characterisation was undertaken.

The cadmium nitrate complex, **2.10**, was isolated from a 1:1 mixture of methanol-dichloromethane as a colourless crystalline solid. The complex was only soluble in donating solvents such as DMSO, and an NMR spectrum showed only free ligand. Combustion analysis gave a 2:1 metal-ligand stoichiometry for **2.10**. Crystals suitable for X-ray structure analysis were obtained by recrystallization from a 1:1 mixture of methanol and water.

Crystal structure of **2.7**

The palladium chloride complex, **2.7**, crystallizes in the orthorhombic space group Pbcn, with half a molecule of **2.1** and half a palladium chloride in the asymmetric unit. The ligand binds the metal through the least hindered nitrogens, shown in figure 2.18, as postulated by Honey. The bond lengths for palladium [Pd1-N3 2.027(2)Å and Pd1-Cl1 2.2925(9)Å] are similar to those of the palladium chloride complex of 2,2′-bipyridine.[60] The molecules of **2.1** are planar (mean deviation of 0.018(5)Å), and pack in alternating columns.

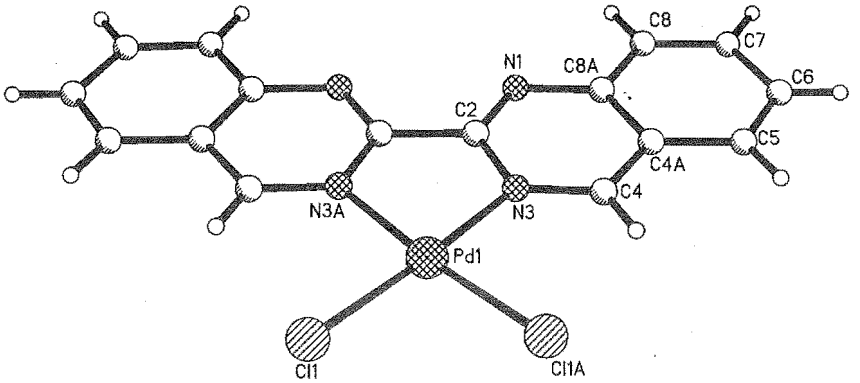


Figure 2.18 Perspective view of **2.7**. Selected bond lengths (Å) and angles (°): Pd1-N3 2.027(2), Pd1-Cl1 2.2925(9), N3-Pd1-N3 80.72(13), N3-Pd1-Cl1A 94.34(7), N3-Pd1-Cl1 174.85(7), Cl1-Pd1-Cl1A 90.63(5).

Crystal structure of **2.8**

The copper(II) chloride complex, **2.8**, crystallizes in the monoclinic space group C2/c. The asymmetric unit contains one molecule of **2.1**, one $CuCl_2$, one third of a water molecule, and disordered DMF molecules with occupancy one half and two thirds. The structure of **2.8**, shown in figure 2.19, is binuclear, with two chlorine atoms bridging the copper atoms, having a Cu···Cu distance of 3.521(2)Å. The ligand, **2.1**, chelates the copper through the least hindered nitrogens. The copper has a square-pyramidal geometry with two nitrogens, monodentate and bridging chloride in the basal plane, and a bridging chloride at the apex. The bond lengths for the coordinating nitrogens are Cu1-N3' 2.025(3)Å and Cu1-N3 2.038(3)Å, with a bite angle of 79.7(1)°. The copper is 0.263(6)Å out of the basal plane towards the apical chlorine. The Cu-Cl bond length for the bridging chloride is 2.270(1)Å and the non-bridging Cu-Cl bond distance is 2.258(1)Å; both are within the normal range for structures of this type.[61]

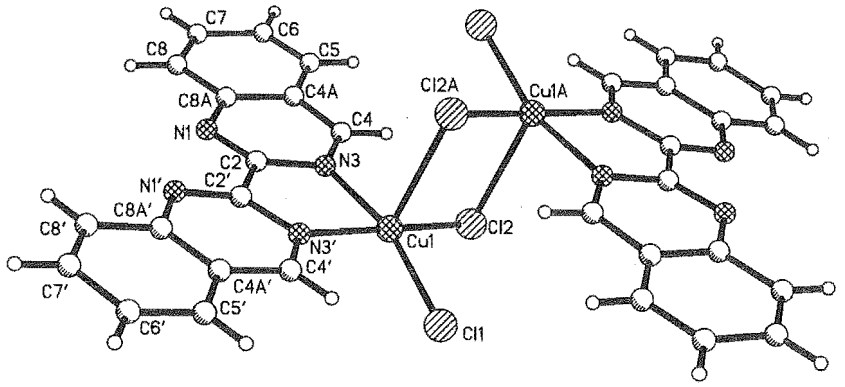


Figure 2.19 Perspective view of **2.8**, with the molecular labelling shown; solvate molecules have been removed for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N3' 2.025(3), Cu1-N3 2.038(3), Cu1-Cl1 2.258(1), Cu1-Cl2 2.270(1), Cu1-Cl2A 2.693(1), N3'-Cu1-N3 79.7(1), N3'-Cu1-Cl1 92.66(8), N3-Cu1-Cl1 163.83(8), N3'-Cu1-Cl2 169.74(8), Cl1-Cu1-Cl2 93.50(4), N3'-Cu1-Cl2A 96.40(8), Cl1-Cu1-Cl2A 104.55(5), Cu1-Cl2-Cu1A 90.01(3).

The binuclear copper units pack in strips, shown in figure 2.20, with the edges of the coplanar aromatic rings adjacent and 3.269(4)Å apart. A partially occupied DMF solvate molecule shares the space between the binuclear units of the strips with a water molecule, the DMF occurring two thirds of the time. The strips organize in layers with the centroid of one of the fused pyrimidine rings of **2.1** 3.471(4)Å above the midpoint of the C4A-C8A

bond of another, indicating a weaker π-π interaction than occurs within the strips. Another DMF molecule lies on a mirror plane in the space between the strips.

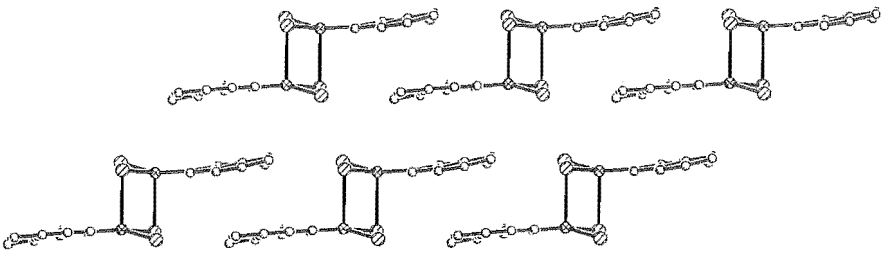


Figure 2.20 View of the packing of **2.8**; DMF, water solvate molecules and hydrogen atoms have been removed for clarity.

Crystal structure of **2.10**

The structure of the cadmium nitrate complex, **2.10**, is mononuclear and crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one cadmium unit, which

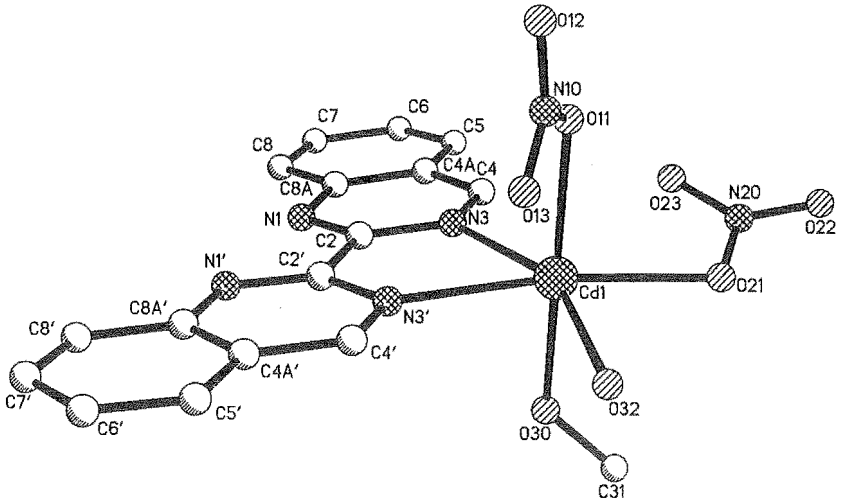


Figure 2.21 Perspective view of the asymmetric unit of **2.10**; hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Cd1-N3' 2.3934(18), Cd1-N3 2.3979(18),Cd1-O30 2.3056(18), Cd1-O21 2.3085(17), Cd1-O11 2.3106(18), Cd1-O32 2.3278(18), N3'-Cd1-N3 69.54(6), O30-Cd1-O21 89.64(6), O30-Cd1-O11 168.28(7), O30-Cd1-O32 87.14(8), O30-Cd1-N3' 89.74(6), O30-Cd1-N3 80.87(7).

is shown in figure 2.21. This 1:1 metal-ligand stoichiometry is different from that found in the elemental analysis of crude **2.10**, and probably represents a reorganization of the structure during recrystallization. In the structure of **2.10**, **2.1** chelates the metal through the least hindered nitrogens. The cadmium is hexacoordinate with the remaining sites occupied by oxygen atoms of two monodentate nitrate anions, and coordinated water and methanol molecules. The bond lengths of the coordinated nitrogens are Cd1-N3' 2.393(2)Å and Cd1-N3 2.398(2)Å, with a bite angle of N3'-Cd1-N3 69.54(6)°.

In the structure the mononuclear cadmium units stack in an alternating pattern, as shown in figure 2.22. The mononuclear units form hydrogen bonded dimers about a centre of inversion, with the non-coordinated nitrogens of **2.1** interacting with the hydroxyl hydrogen of the coordinated methanol. The bifurcated hydrogen is slightly closer to one side of **2.1**, with H30A 2.30(3)Å from N1 and 2.55(3)Å from N1'. These hydrogen bonds distort the coordination geometry of the cadmium by pulling the methanol towards the most hindered nitrogens of the adjacent molecule of **2.1**, giving an O30-Cd1-O11 angle of 168.28(7)°. The dimers arrange with the coplanar rings of **2.1** 3.369(6)Å apart.

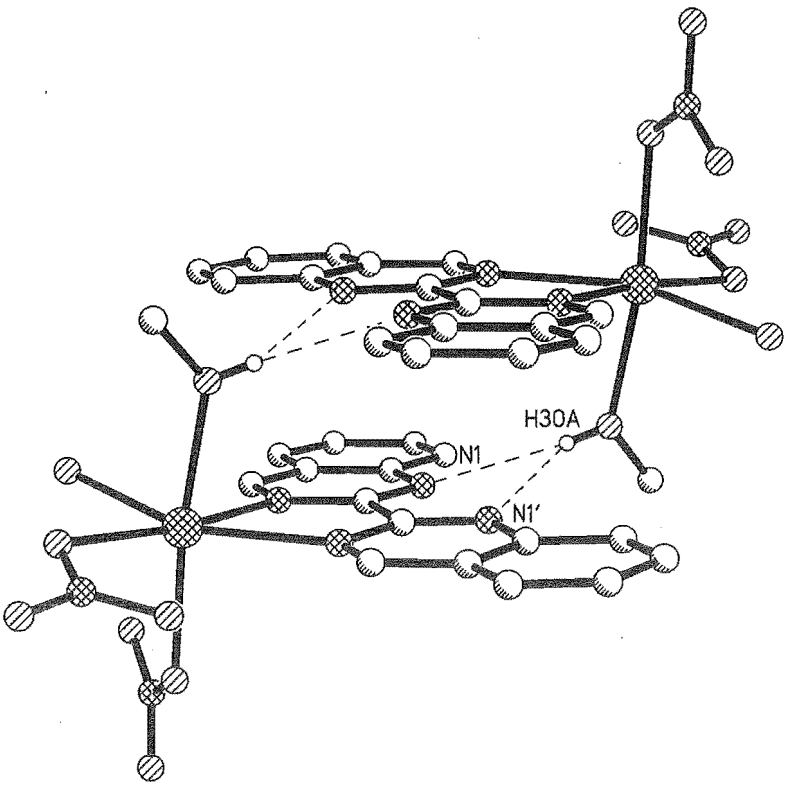


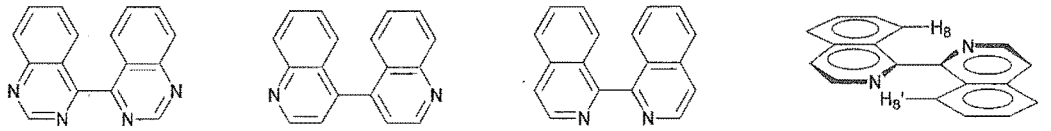
Figure 2.22 Perspective view of the packing of **2.10**, with the hydrogen bonding of H30A shown.

Further intermolecular aggregation occurs through hydrogen bonds from each of the coordinated water hydrogen atoms to oxygens of nitrate anions of adjacent molecules. Hydrogen bonds of this sort are common in crystal structures of coordination and organometallic compounds, particularly when hydrogen atoms bound to donating elements such as oxygen or nitrogen are present.[62] These can be found coordinated, as is the case for **2.10**, or as solvate molecules.

2.5 4,4′-Biquinazoline

The coordination chemistry of 4,4′-biquinazoline (**2.2**) (fig 2.23(a)) has not been investigated, even though this potential ligand was first synthesised in 1943.[63] The molecule represents a benzo-fused analogue of 4,4′-bipyrimidine, and combines chelating and bridging and binding modes in the same molecule.

The potential ligand **2.2** can be thought of as a combination of the binding geometries of 4,4′-biquinoline (fig 2.23(b)) and 1,1′-biisoquinoline (fig 2.23(c)). The chelating site of **2.2** has structural similarities to that of 1,1′-biisoquinoline, which is non-planar due to the steric interaction of H8 and H8′ (fig 2.23(d)). The restricted rotation of the isoquinoyl groups about the inter-ring bond leads to the formation of a mixture of atropisomers.[¶] The coordination chemistry of 1,1′-biisoquinoline is dominated by this non-planarity, which, in



(a) (b) (c) (d)

Figure 2.23

combination with enantiomeric metal precursors, forms mixtures of diastereomeric complexes.[65] The non-planarity distorts the chelate ring of the complexes formed,[66] and

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[¶] Atropisomers are molecules that posses a chiral axis that is maintained by restricted rotation about a bond, usually due to steric congestion. The molecules posses a helical turn and, therefore, the mirror images are enantiomeric.[64] Biphenyls and related molecules (eg biheterocycles) with sufficiently large adjacent groups display atropisomerism.

allows 1,1′-biisoquinoline to bridge two metals.[67] The crystal structure of **2.2** above has shown that the molecule is twisted in this way, and formation of complexes from this non-planar ligand could allow interesting structures to form. The coordination chemistry of the potential ligand 4,4′-biquinoline has not been investigated.

2.5.1 Coordination chemistry of 2.2

The coordination chemistry of **2.2** was investigated by the formation of complexes with $AgNO_3$ (**2.11**), $PdCl_2$ (**2.12**), and $CuCl_2$ (**2.13**). The preparation of the silver nitrate complex, **2.11**, involved the reaction of **2.2** with $AgNO_3$ in a 1:1 mixture of acetone-methanol. The white precipitate that was isolated analysed with a 2:3 ligand-metal stoichiometry. This stoichiometry might indicate the formation of various structures, including oligomeric or polymeric species. A 2:3 ligand-metal stoichiometry was observed in three complexes of silver with 2,2′-dimethyl-4,4′-bipyrimidine, a molecule similar to **2.2**. These complexes were polymeric, with the formation of 3-D arrays, and two 2-D sheets; the ligands were tetradentate in these complexes, with both chelating and bridging sites occupied.[42] Despite the intriguing stoichiometry of this complex, no crystals of **2.11** were obtained from this reaction.

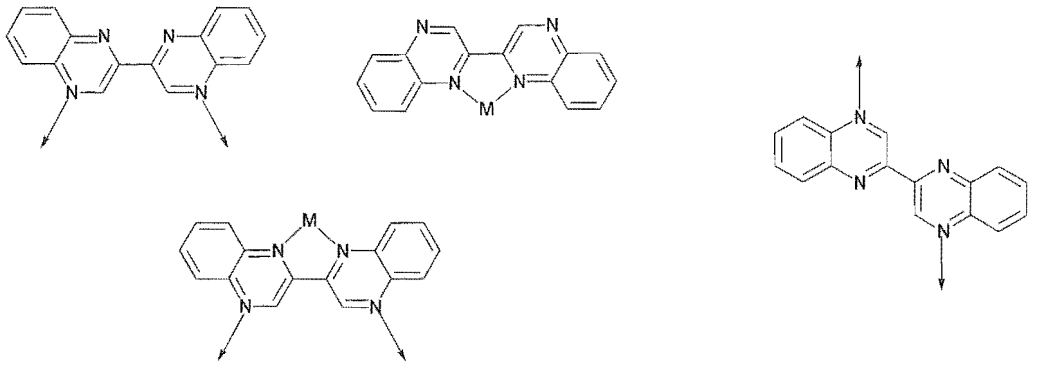
The palladium chloride complex, **2.12**, was obtained from the reaction of **2.2** in acetonitrile with Li_2PdCl_4 in methanol. The yellow complex isolated analysed as $[PdCl_2.(\mathbf{2.2}).3H_2O]$, and was insoluble in common solvents. This might indicate a polymeric structure for **2.12**, with no further analysis being undertaken.

The reaction of **2.2** with copper(II) chloride in a 1:1 mixture of acetonitrile-methanol gave a green crystalline precipitate, **2.13**. The crystals formed were too small for X-ray structure analysis, and analysed with a 1:1 ligand-metal stoichiometry. No further analysis was undertaken.

2.6 2,2′-Biquinoxaline

2,2′-Biquinoxaline (**2.3**) was first synthesised 64 years ago,[68] and has been used as a ligand for the determination of trace metal concentration by spectrochemical methods.[69] Apart from this, the coordination chemistry of **2.3** has largely been ignored. The possible coordination modes of **2.3** depend on its conformation. Assuming **2.3** is planar, a *cisoid* conformation would allow chelation or bridging at a 60° angle or the combination of both,

as shown in figure 2.24(a). If **2.3** is planar, then a *transoid* conformation would allow linear bridging through the least hindered nitrogen atoms of **2.3**, as shown in figure 2.24(b). It was found above that in the solid state **2.3** adopts a *trans*-planar conformation.



(a) **(b)**

Figure 2.24 Possible binding modes for **2.3**. **(a)** *cisoid*-**2.3**, **(b)** *transoid*-**2.3**.

2.6.1 Coordination chemistry of 2.3

The coordination chemistry of **2.3** was investigated with the synthesis of complexes using $AgNO_3$ (**2.14**), $PdCl_2$ (**2.15**), $CuCl_2$ (**2.16**), CuI (**2.17**), $Cd(NO_3)_2$ (**2.18**), and $Cu(PPh_3)_2NO_3$ (**2.19**). The silver nitrate complex, **2.14**, was isolated as orange crystals in good yield (74%). Analysis of these crystals gave a composition of [$AgNO_3$.(**2.3**)]. This could indicate a mononuclear or a polymeric structure, and an X-ray structure analysis of these crystals was undertaken.

The palladium chloride complex, **2.15**, was isolated as a brown-black solid. Despite numerous attempts to get elemental analysis and NMR spectra of the complex, no results could be obtained, and no further analysis was undertaken.

Reaction of **2.3** with $CuCl_2$ in a 1:1 solution of dichloromethane-methanol produced a green/black crystalline solid, **2.16**, which analysed as [$CuCl_2$.(**2.3**).MeOH.$\frac{1}{2}H_2O$]. This could indicate a polymeric structure, or an oligomeric structure similar to that of **2.16** above. Thus, a single crystal structure analysis was undertaken to resolve this. Crystals suitable for X-ray structure determination were grown by layering a methanol solution of $CuCl_2$ onto a dichloromethane solution of **2.3**.

The copper(I) iodide complex, **2.17**, was isolated as a black precipitate from the reaction of CuI and **2.3** in a 1:1 solution of acetonitrile/acetone. This complex analysed as M_5L_2, which could indicate various oligomeric or polymeric structures. Recrystallization

of the black crystals from DMSO afforded large red plates suitable for X-ray structure analysis.

The orange powder (**2.18**) isolated in good yield (81%), from the reaction of **2.3** with cadmium nitrate. This analysed as $[Cd(NO_3)_2.(\mathbf{2.3})]$, was extremely insoluble, possibly indicating a polymeric structure. No further analysis was undertaken.

The reaction of **2.3** with copper(I) bistriphenylphosphine nitrate in methanol produced a red solution which gave large red crystals of **2.19** on standing. The red crystals analysed as $[(Cu(PPh_3)_2NO_3).(\mathbf{2.3}).MeOH]$, and were soluble in acetonitrile. An NMR spectrum showed only free ligand, and an electrospray mass spectrum indicated the presence of $[CuPPh_3.(\mathbf{2.3})]^+$. To determine the composition of **2.19** an X-ray crystal structure was undertaken.

Crystal structure of **2.14**

The silver nitrate complex **2.14** has a two-dimensional polymeric structure, and crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains two independent half molecules of the ligand, **2.3**, and one silver nitrate. The ligands both lie with centres of inversion at the midpoint of the inter-ring bond and are consequently planar, with mean deviations of 0.050(4)Å and 0.027(4)Å. The molecules of **2.3** are independent and at an angle of 85.9(3)° to one another. The ligands are in a *trans*-planar conformation, and coordinate the silver through the least hindered nitrogens, as shown in figure 2.25. They bridge the silver atom in different directions, giving a pleated sheet. The ligands bridge the silver atoms at distances of 10.246(4)Å and 10.086(4)Å. The geometry of the silver atom can best be described as distorted tetrahedral, with an angle of 140.85(8)° between the nitrogens of the two ligands. The bond lengths for the coordinated nitrogens are Ag1-N4' 2.303(2)Å and Ag1-N4 2.308(2)Å.

The silver atoms are also bridged by nitrate anions, shown in figure 2.26, which separate them by a distance of 5.204(2)Å. The coplanar rings of both the independent ligands stack in different directions, with the rings 3.585(4)Å and 3.462(4)Å apart, indicating weak π-π stacking interactions.

There is also a C-H···O interaction between the oxygen atom of the nitrate anion and an aromatic hydrogen of **2.3**. Such interactions are defined by D (fig 2.27), the distance between the donor atom and the acceptor atom, and θ, the angle between the donor,

hydrogen and acceptor atoms. It has been proposed that D values of 2.5 – 4Å and θ values of 150 – 180° can be structurally significant.[4]

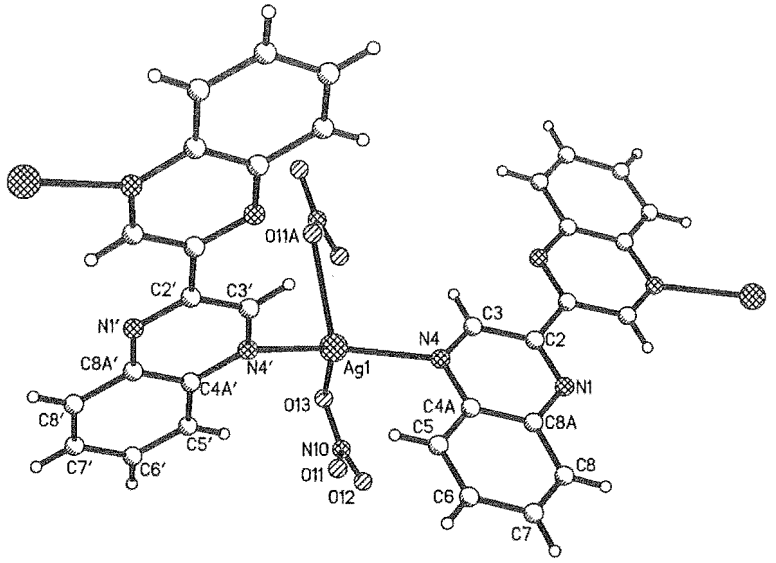


Figure 2.25 Perspective view and atom labelling of **2.14**, with the molecular labelling shown. Selected bond lengths (Å) and bond angles (°): Ag1-N4' 2.303(2), Ag1-N4 2.308(2), Ag1-O11A 2.501(3), Ag1-O13 2.590(2), N4'-Ag1-N4 140.85(8), N4-Ag1-O11 106.86(9), N4'-Ag1-O13 119.92(8), N4-Ag1-O13 91.08(8), O11A-Ag1-O13 116.16(8), C3'-N4'-Ag1 116.6(2).

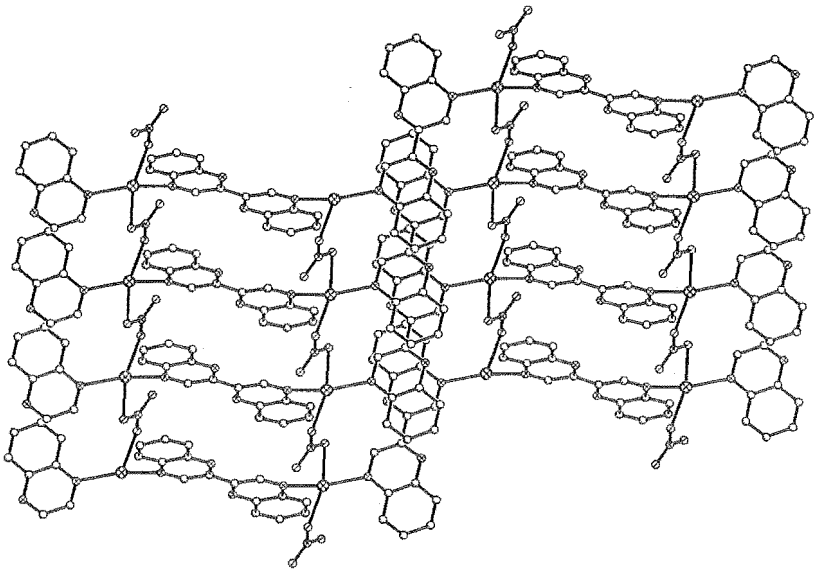


Figure 2.26 View of the two dimensional polymeric nature of **2.14**, showing the bridging nitrate counterions and π-π stacking between the molecules of **2.3**.

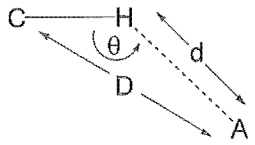


Figure 2.27 Representation of hydrogen bonding between C-H and a H-acceptor atom.

There is such an interaction between the uncoordinated oxygen of the nitrate anion, O12, and H7′ of another polymeric chain (fig 2.28), with D and θ values of 3.401(4)Å and 156°. This indicates that the edge of the molecule of **2.3** is adjacent to the nitrate anion. As a consequence, there are no significant edge-to-face interactions between the aromatic rings of **2.3**.

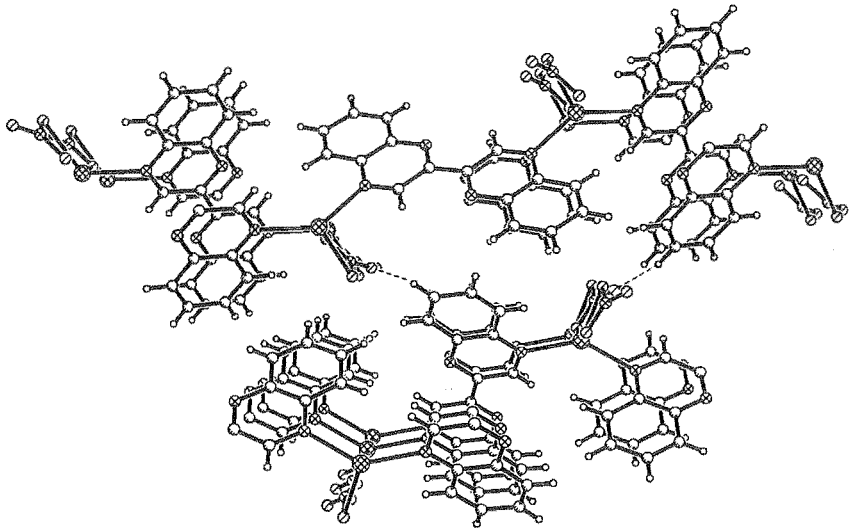


Figure 2.28 Perspective view down the *a*-axis of the unit cell, showing the hydrogen bonding between H7' of one polymeric chain and O12 of another.

Crystal structure of **2.16**

The complex **2.16** is a one-dimensional coordination polymer, shown in figure 2.29, which crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of **2.3**, with one copper(II) chloride and one coordinated methanol. The ligand, **2.3**, is in a *trans*-planar conformation (mean deviation 0.026(5)Å) and bridges two copper atoms through the least hindered nitrogens, giving a Cu···Cu separation of 9.549(6)Å. The geometry around the copper atom is slightly distorted square pyramidal, with *trans*-chlorine atoms and *trans*-nitrogens of **2.3** in the basal plane. The copper atom lies

0.391(5)Å above the basal plane. The bond distances for the nitrogen atoms of **2.3** are Cu1-N4 2.030(3)Å and Cu1-N4' 2.038(3)Å, with an angle of N4-Cu1-N4' 176.1(1)°.

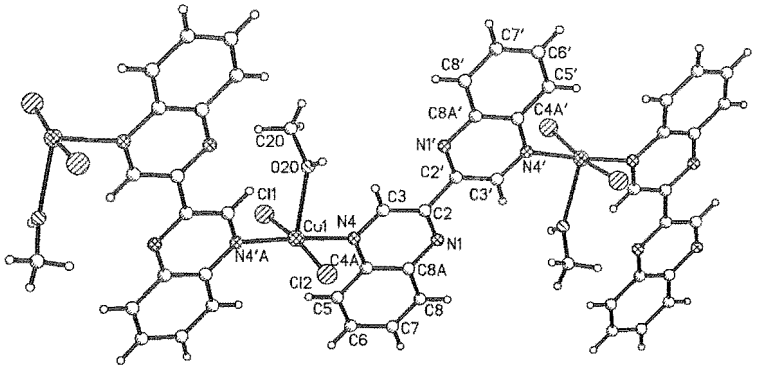


Figure 2.29 Perspective view of **2.16**, with the atomic labelling shown. Selected bond lengths (Å) and bond angles (°): Cu1-N4 2.030(3), Cu1-N4'A 2.038(3), Cu1-Cl2 2.259(1), Cu1-Cl1 2.277(1), Cu1-O20 2.390(3), N4-Cu1-N4'A 176.1(1), N4-Cu1-Cl2 89.1(1), N4'A-Cu1-Cl2 88.12(9), N4-Cu1-Cl1 91.02(9), N4'A-Cu1-Cl1 91.26(9), Cl2-Cu1-Cl1 170.96(4), N4-Cu1-O20 91.5(1), N4'A-Cu1-O20 91.6(1), Cl2-Cu1-O1 97.92(8), Cl1-Cu1-O20 91.11(8).

The polymer propagates along the *b*-axis of the unit cell in a zig-zag pattern. The polymer chains arrange with the molecules of **2.3** stacked and coplanar, the edge of each quinoxaline ring of **2.3** lying above another at a distance of 3.281(5)Å. There is also a hydrogen bond between the hydroxyl hydrogen of the methanol and a chlorine atom of an adjacent chain, as shown in figure 2.30. This satisfies the conditions for a hydrogen bond, with D = 3.091(3)Å and θ = 161(4)°.

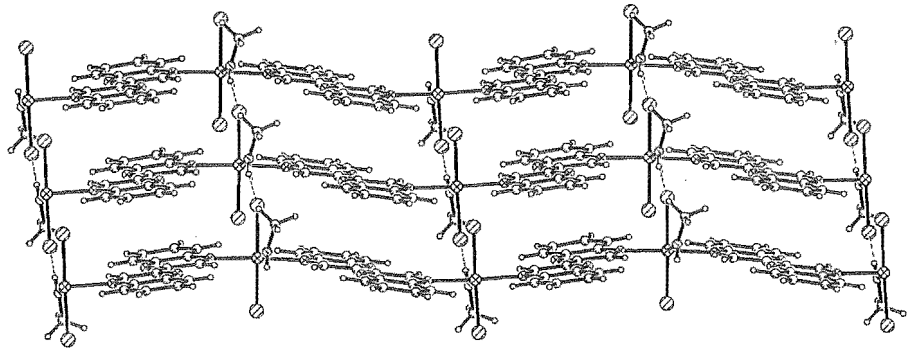


Figure 2.30 Perspective view of the polymeric chains of **2.16**, showing the hydrogen bonds between H1 and Cl1.

Crystal structure of **2.17**

The copper(I) iodide complex, **2.17**, crystallizes in the triclinic space group P-1, with one molecule of **2.3** and one copper(I) iodide in the asymmetric unit. This 1:1 metal-ligand stoichiometry is different from that found in the elemental analysis of crude **2.17**, and probably represents a reorganization of the structure during crystal growth in DMSO. The structure **2.17**, shown in figure 2.31, is binuclear, with the copper atoms bridged by iodine atoms, giving a Cu···Cu distance of 2.712(1)Å. In this structure **2.3** chelates the copper through the most hindered nitrogen atoms, and this restricts **2.3** to be planar, with a mean deviation of 0.062(5)Å from planarity. The copper has a distorted tetrahedral geometry, with Cu-N bond lengths of 2.095(2)Å and 2.114(2)Å, and Cu-I bond lengths of 2.5737(9)Å and 2.6819(9)Å. The two molecules of **2.3** are coplanar, but are stepped with a distance of 2.338(5)Å between the planes. This stepping pulls the copper out of the coordination plane of **2.3** by 0.497(5)Å.

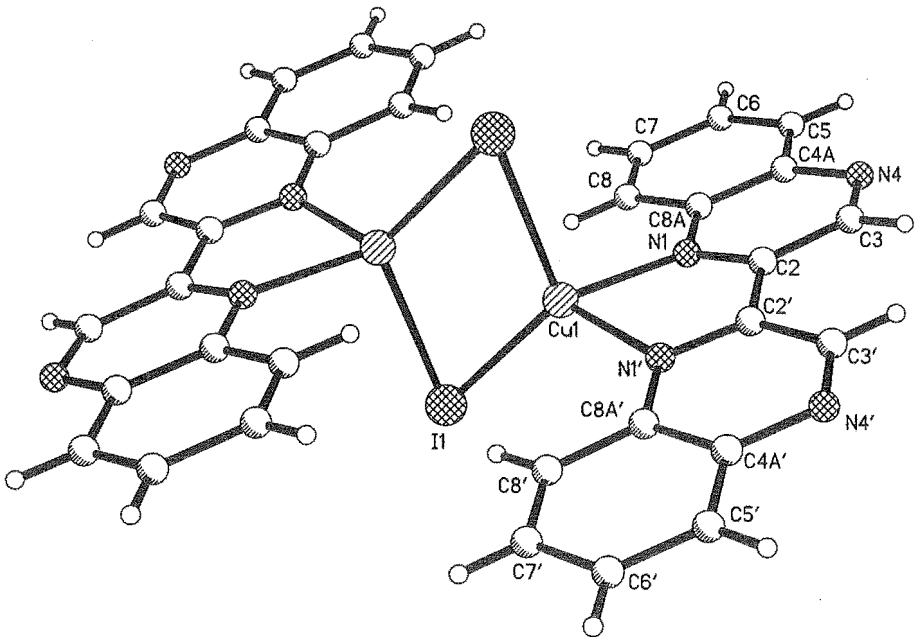


Figure 2.31 Perspective view of **2.17**, with the asymmetric unit labelled. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.095(2), Cu1 N1' 2.114(2), Cu1-I1 2.5737(9), Cu1-I1 2.6819(9), N1-Cu1-N1' 78.65(9), N1-Cu1-I1 125.97(6), N1'-Cu1-I1 120.73(6), N1-Cu1-I1 99.61(6), N1'-Cu1-I1 106.39(6), I1-Cu1-I1 117.90(1).

The binuclear units, shown in figure 2.32, stack with the C4A – C8A ring of one molecule coplanar and 3.389(5)Å above the C4A' – C8A' ring of an adjacent ligand, and vice versa. The rings of adjacent stacks also lie coplanar, with C6 of one ligand lying 3.275(5)Å above the centroid of the C4A – C8A ring of another. The structure of **2.17** is similar to the copper(I) iodide complex of 2,9-dimethyl-1,10-phenanthralene, which has similar bond lengths and geometry. The Cu···Cu distance of 3.024(2)Å is slightly longer, possibly due to the increased steric bulk of 2,9-dimethyl-1,10-phenanthralene.[70]

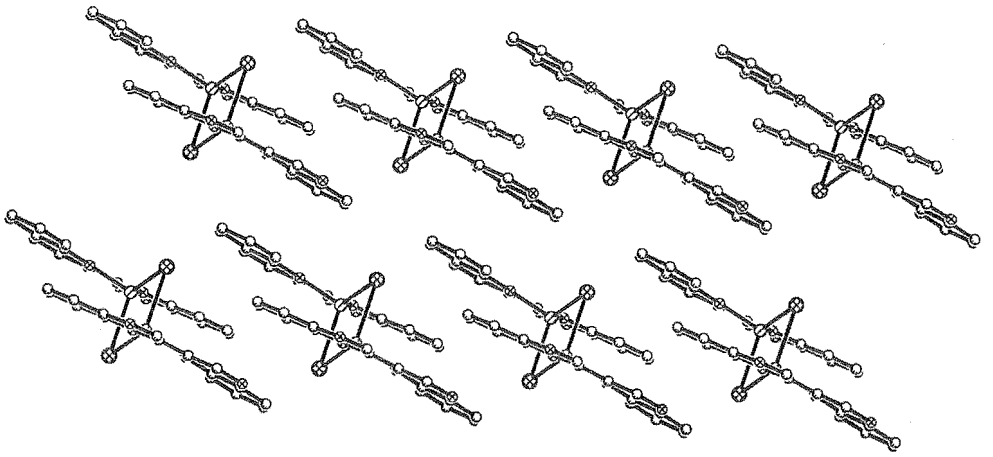


Figure 2.32 View of the packing of **2.17**, with hydrogen atoms removed for clarity.

Crystal structure of **2.19**

The structure of **2.19**, shown in figure 2.33, consists of **2.3** chelating a copper atom with two triphenylphosphine moieties attached. The asymmetric unit of the centrosymmetric triclinic structure also contains a highly disordered nitrate counterion, with methanol and water solvate molecules. The ligand, **2.3**, is coordinated to the copper atom through the most hindered nitrogens, and is in a *cis*-planar conformation (mean deviation from planarity 0.16(1)Å for the non-hydrogen atoms). The bond distances between the nitrogen and the metal are N1A-Cu1 2.101(6)Å and N1B-Cu1 2.102(6)Å with a bite angle of 78.1(2)°. One of the phenyl groups of a triphenylphosphine points towards the plane of **2.3**, with the closest approach made by C6, 3.270(8)Å above the **2.3**.

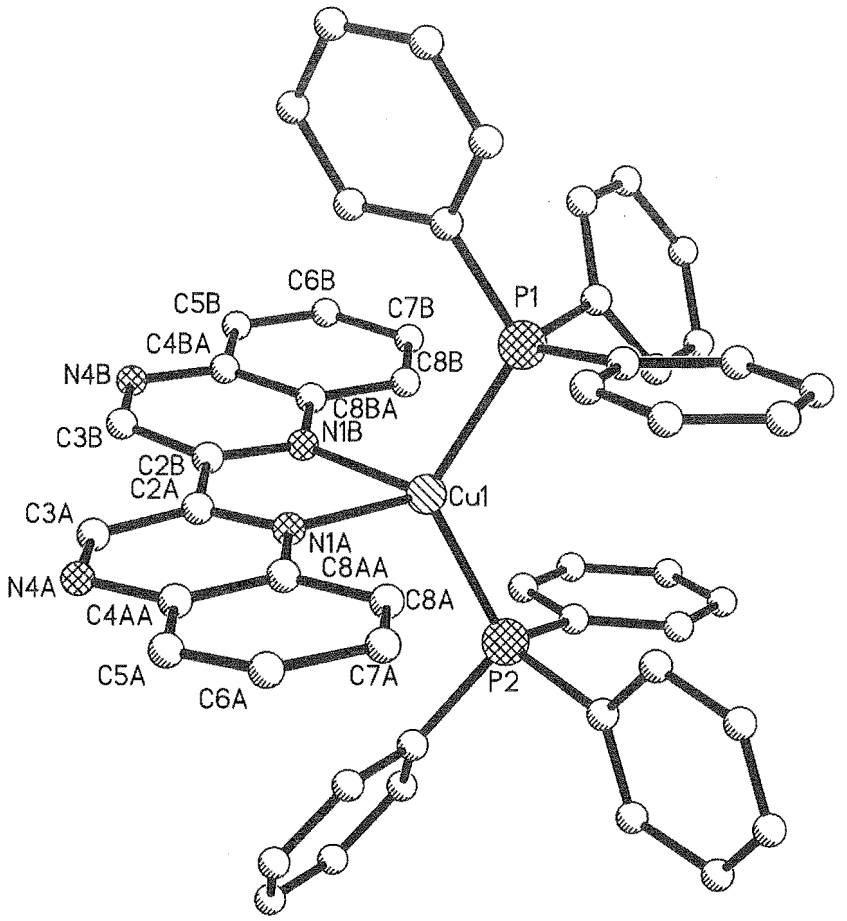


Figure 2.33 Perspective view of **2.19**, with the labelling of **2.3** shown. Disordered nitrate, solvate molecules and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1A 2.099(4), Cu1-N1B 2.099(4), Cu1-P1 2.279(2), Cu1-P2 2.292(2), N1A-Cu1-N1B 78.00(2), N1A-Cu1-P1 114.7(2), N1B-Cu1-P1 107.8(2), N1A-Cu1-P2 112.3(2), P1-Cu1-P2 122.26(6).

The aryl rings of triphenylphosphine groups can interact in crystal structures via face-to-face and edge-to-face interactions. A so-called 'hexa-aryl embrace' involves two PPh_3 with approximate S_3 symmetry interacting via six edge-to-face interactions between interleaved phenyl rings. Such interactions are relatively common among complexes which contain coordinated PPh_3 groups (30% of structures in the CSD which contain M-PPh_3) and complexes crystallized as PPh_4^+ salts (60% of structures in CSD which contain PPh_4^+). Such interactions are defined by the distance between phosphorus atoms (typically 6.4 –

7.5Å) and the colinearity of the groups, calculated as half the sum of the P···P-M and M-P···P angles (typically 160° – 180°).[71]

One of the triphenylphosphine groups of **2.19** is involved in a 'hexa-aryl embrace' type interaction, as shown in figure 2.34. The PPh_3 groups, related by a centre of symmetry, are close, with a P···P distance of 6.422(6)Å, and are approximately colinear [170.4(2)°]. The closest interactions of the 'hexa-aryl embrace' occur between H6 of the aryl groups of the triphenylphosphine and the C1-C6 bond, with the distances within the range 2.708(8) – 2.791(8)Å. The second PPh_3 group of **2.19**, while not involved in a 'hexa-aryl embrace', is interacting with another PPh_3 group via an edge-to-face interaction. The closest approach involves H5F which lies 2.64(1)Å away from the centre of the C5H-C6H bond.

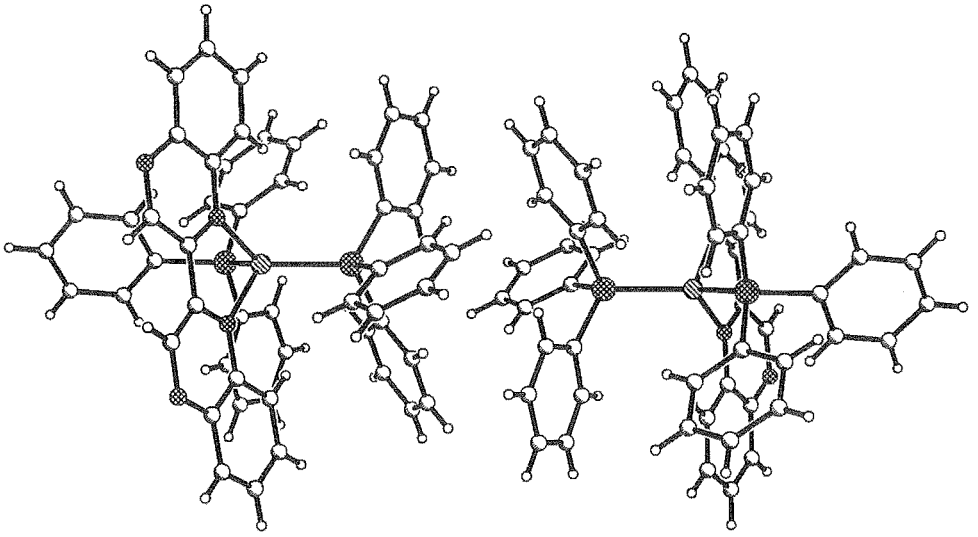


Figure 2.34 Perspective view of the 'hexa-phenyl embrace' between the PPh_3 groups in the structure of **2.19**.

The bulky triphenylphosphine groups of **2.19** preclude many of the face-to-face and edge-to-face interactions between ligand molecules that have been seen in the previous compounds. However, the mononuclear complexes related by a centre of inversion arrange with the edges of **2.3** coplanar and 3.127(8)Å apart.

The molecules pack into columns along the *c*-axis of the unit cell, leaving large voids along this axis, as shown in figure 2.35. These voids contain the disordered solvent molecules and nitrate counterions.

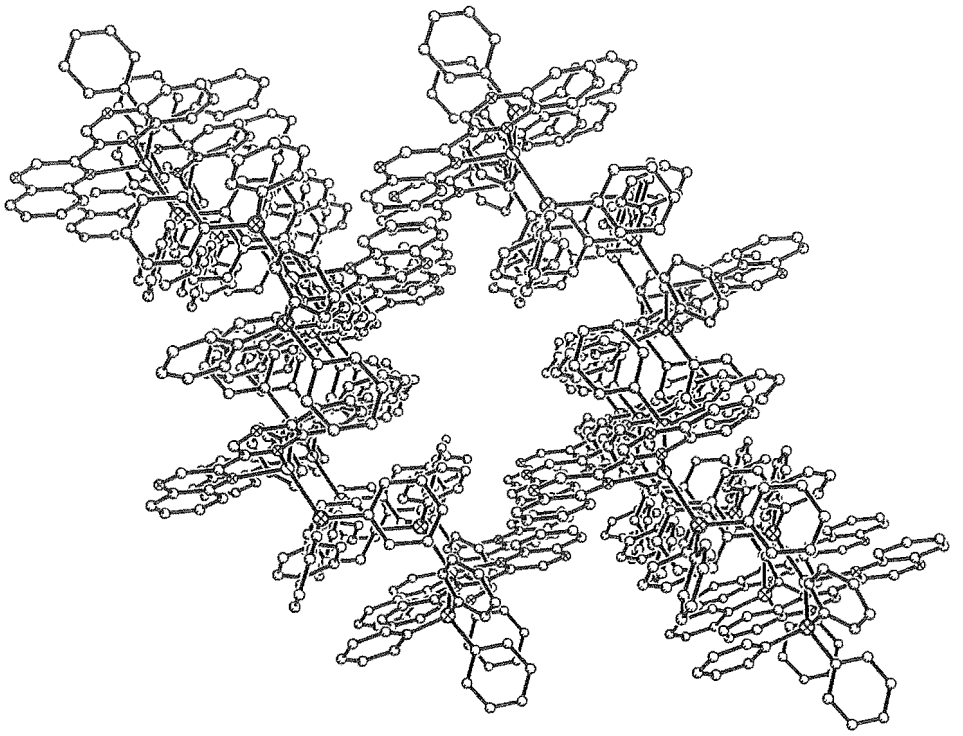


Figure 2.35 Perspective view of the packing of **2.19** looking down the *c*-axis, showing the solvent and counterion containing voids. Disordered solvate molecules, counterions and hydrogen atoms have been removed for clarity.

2.7 3,3′-Biquinoline

No coordination chemistry of 3,3-biquinoline (**2.4**) has been reported since it was first synthesised over 70 years ago.[72] The non-benzofused molecule 3,3′-bipyridine represents a less sterically hindered, but structurally similar ligand to **2.4**. The coordination chemistry of 3,3′-bipyridine with copper(I) X^- (X = BF_4, PF_6) and nickel(II) nitrate has been investigated. The copper(I) complex formed has an interpenetrating adamantoid structure, with non-planar 3,3′-bipyridine units bridging two copper atoms.[73] The nickel(II) nitrate complex forms part of a so-called 'hybrid organic-inorganic material' and has a three-dimensional polymeric structure, which has large cavities containing $[Mn_4O_{14}]^{4-}$ clusters.[74] These represent the only X-ray crystallographic studies of coordination complexes involving 3,3′-bipyridine.

Similar to the other biheterocycles described above, the conformation of **2.4** in any complex will dictate the structure formed. The ligand is less likely to be planar than in the ligands above, due to repulsive C-H···H-C interactions between the groups adjacent to the inter-ring bond (see above). However, if planarity is assumed then the possible bridging modes of **2.4** are shown in figure 2.36. The ligand, if *transoid*, can form a linear bridge between two metals, and, if *cisoid*, can bridge two metals at an angle of 60°. The orientation of the nitrogen atoms of **2.4** means that this molecule is incapable of chelating a metal atom.

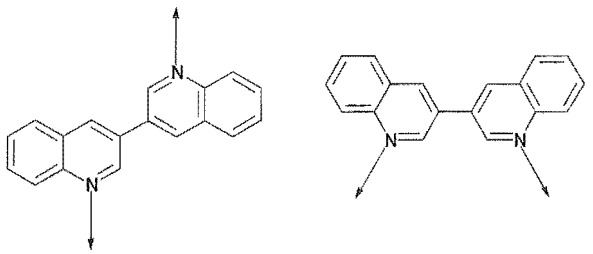


Figure 2.36 Possible bridging of transition metals by **2.4** through the heteroatoms.

2.7.1 Coordination chemistry of 2.4

The coordination chemistry of **2.4** was investigated with the formation of complexes with $AgNO_3$ (**2.20**), $PdCl_2$ (**2.21**), $Cu(NO_3)_2$ (**2.22**), CuI (**2.23**) and $CdCl_2$ (**2.24**). Reaction of **2.4** with silver nitrate in methanol gave a white powder. This complex could not be analysed due to transformation of the white solid into a black powder within minutes. This occurred even when the solvent was varied, and the reaction was done in the absence of light.

The palladium chloride and copper(II) nitrate complexes, **2.21** and **2.22**, were prepared by reaction of **2.4** dissolved in dichloromethane with methanol solutions of Li_2PdCl_4 and $Cu(NO_3)_2$, respectively. The complexes analysed as [M.(**2.4**).nH$_2$O] with n=3 for the palladium chloride complex and n=½ for the copper(II) nitrate complex. Both of the complexes were insoluble in common solvents, and no further analysis was undertaken.

The reaction of **2.4** with copper(I) iodide in acetonitrile gave a yellow powder in modest yield. This complex, **2.23**, analysed with an intriguing M_5L_3 stoichiometry, and was insoluble in common solvents. Despite numerous attempts no crystals of suitable quality for X-ray could be grown, and no further analysis was undertaken.

The cadmium chloride complex, **2.24**, was prepared by reacting cadmium chloride with **2.4** in a 1:1 mixture of dichloromethane and methanol. The white powder formed

analysed with a 2:3 ligand-metal stoichiometry. No further analysis was undertaken due to the insolubility of **2.24** in common solvents.

Thus, none of the above complexes furnished crystals suitable for X-ray crystallography and hence complexes of this ligand remain structurally uncharacterised.

2.8 2,2′-Bi-1,5-naphthyridine

The coordination chemistry of 2,2′-bi-1,5-naphthyridine (**2.5**) has not been investigated, and indeed no chemistry of **2.5** has been investigated since it was first synthesised over 40 years ago.[53] Other binaphthyridines have been used as ligands in coordination chemistry, and the structurally similar ligand 2,2′-bi-1,6-naphthyridine was the subject of a recent study.[75] The authors identified this ligand as being a 'functionalised 2,2′-bipyridine', with both chelating and bridging domains. The reaction of this with divalent metals (Co, Zn, Cd) in the presence of KSCN produced interpenetrated coordination nets, while reaction with Cu(I) produced a helical coordination polymer.

The coordination chemistry of **2.5** depends on its conformation, with the possible bridging modes shown in figure 2.37. If the ligand is in a *trans*-planar conformation it can form linear, stepped bridging structures. If it is in a *cis*-planar conformation it forms an angular bridging ligand, which can bind metal components at an angle of 60°. When in this *cis*-planar conformation, **2.5** can also chelate a metal through the two most hindered nitrogens. In the *trans*-planar **2.5**, however, the adjacent C-H group provides steric hinderance to binding at this site.

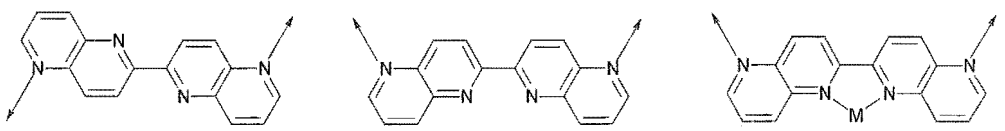


Figure 2.37 Possible bridging of transition metals by **2.5** through the heteroatoms.

2.8.1 Coordination chemistry of 2.5

Complexes of **2.5** were prepared with $AgBF_4$ (**2.25**), $PdCl_2$ (**2.26**), and $Cu(NO_3)_2$ (**2.27**). The silver tetrafluoroborate complex, **2.25**, was isolated as yellow crystals by diffusion of pentane into an acetonitrile solution containing $AgBF_4$ and **2.5**. This complex

analysed with an intriguing M_4L_3 stoichiometry [$(AgBF_4)_4.(\mathbf{2.5})_3.2CH_3CN$], and it was therefore decided to undertake a single crystal structure analysis of these crystals.

The palladium chloride complex, **2.26**, was prepared by the reaction of **2.5** with Li_2PdCl_4. The yellow complex analysed with a 1:1 metal-ligand stoichiometry. The complex was insoluble in common solvents. No further analysis was undertaken.

The copper(II) nitrate complex, **2.27**, was isolated as green crystals from an acetonitrile solution of **2.27**. These crystals analysed as [$Cu(NO_3)_2.\mathbf{2.5}$], and were subjected to a single crystal structure analysis.

Crystal structure of **2.25**

The complex crystallizes in the triclinic space group P-1, with two silver tetrafluoroborates and one and a half molecules of **2.5** in the asymmetric unit. The structure of **2.25**, shown in figure 2.38, is a remarkable discrete tetranuclear complex with four silver atoms bridged by three molecules of **2.5**. The central ligand lies on a centre of inversion and hence has a *trans*-planar conformation. It bridges two silver atoms through the least hindered nitrogens at a distance of 12.759(7)Å. The two remaining ligands are in a *cis*-planar conformation, and chelate one silver atom and bridge another through the least hindered nitrogens at a distance of 7.716(7)Å. The silver atom, Ag2, is coordinated by two molecules of **2.5** with bond distances of Ag2-N5C 2.175(4)Å and Ag2-N5B 2.181(4), in a distorted linear geometry [N5C-Ag2-N5B 167.9(1)°]. The silver atom, Ag1 is chelated by one molecule of **2.5**, with bond lengths of Ag1-N1A 2.293(4) and Ag1-N1B 2.292(4), and coordinated by a molecule of acetonitrile with an overall trigonal-planar geometry. The tetranuclear structure is remarkably planar, with a mean deviation of only 0.092(7)Å for the non-hydrogen atom meanplane.

The tetranuclear units arrange in a coplanar stack, with two linear Ag2 atoms adjacent to one another, as shown in figure 2.39. The silver atoms are separated by a distance of 3.556(4)Å, possibly indicating a weak interaction.[22,76] This means that the units are offset by one molecule of **2.5**, so that *cis*-planar ligands stack atop *trans*-planar ligands, and vice versa. The midpoint of the C6A-C7A bond is above the centre of the outside ring of the *trans*-**2.5** ring; the distance between the planes of the tetranuclear units is 3.258(7)Å, indicating a strong π-π interaction. Further intermolecular aggregation occurs between the stacks of molecules via face-to-face interactions of the planar aromatic stacks.

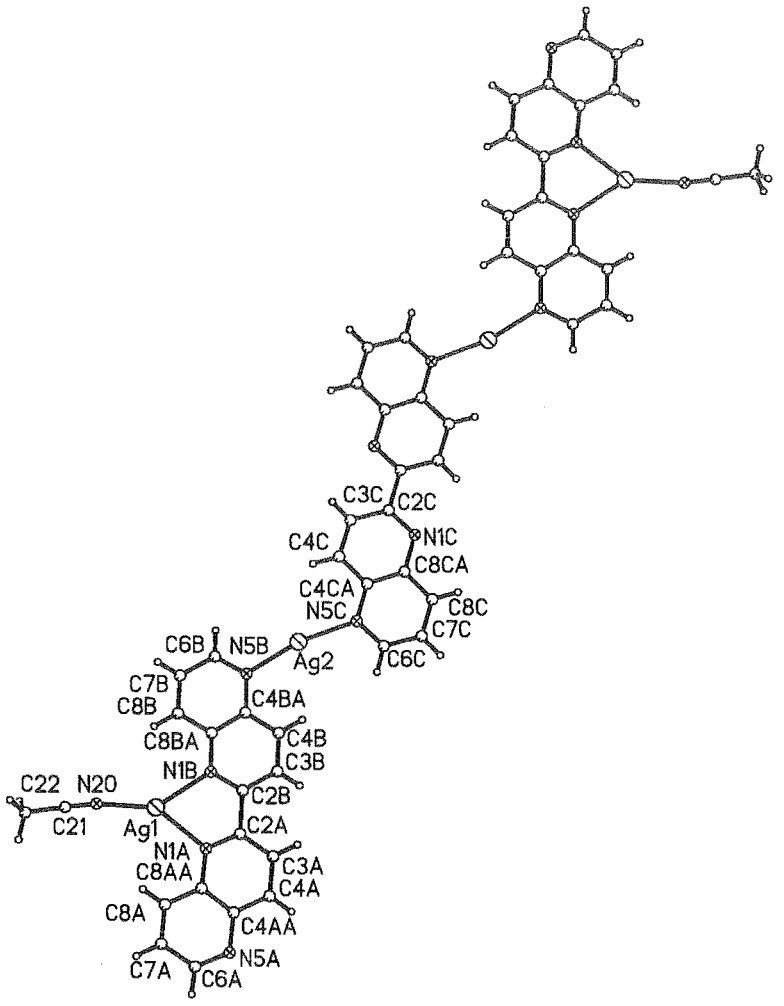


Figure 2.38 Perspective view of **2.25**, with the asymmetric unit labelled. Tetrafluoroborate counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N20 2.114(4), Ag1-N1A 2.293(4), Ag1-N1B 2.292(4), Ag2-N5C 2.175(4), Ag2-N5B 2.181(4), N20-Ag1-N1A 144.9(1), N20-Ag1-N1B 142.8(1), N1A-Ag1-N1B 72.3(1), N5C-Ag2-N5B 167.9(1).

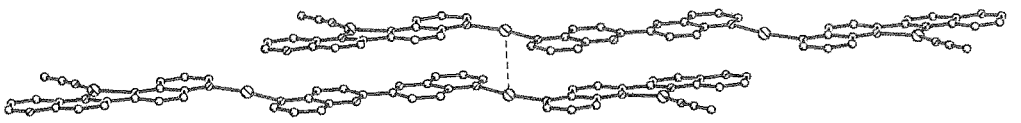


Figure 2.39 Perspective view of the layering of tetranuclear units in **2.25**, with the Ag-Ag interaction shown. Hydrogen atoms and tetrafluoroborate counterions have been removed for clarity.

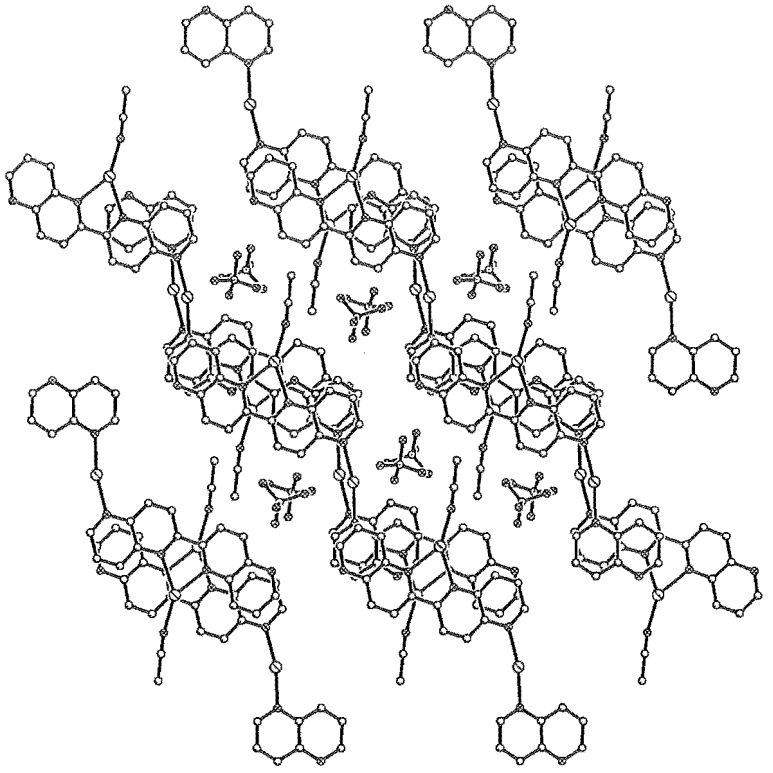


Figure 2.40 View of **2.25** down the *b*-axis of the unit cell, showing tetrafluoroborate counterions. Hydrogen atoms have been omitted for clarity.

The stacked tetranuclear units arrange as shown in figure 2.40. The coordinated acetonitrile molecules and tetrafluoroborate counterions occupy the spaces between these sheets. The tetrafluoroborate counterions are held in place via numerous weak C-H···F interactions, the shortest being 2.40(5)Å between H6A and F13.

Crystal Structure of **2.27**

The complex crystallizes in the triclinic space group P-1, with one molecule of **2.5** and one copper(II) nitrate in the asymmetric unit. The mononuclear structure of **2.27** is shown in figure 2.41, with one molecule of **2.5** chelating one atom of copper through the most hindered nitrogen atoms. The ligand, **2.5**, is held in a *cis*-planar conformation, with a mean deviation of 0.041(5)Å from planarity. The nitrate anions chelate the copper atom asymmetrically, with each having a short bond [Cu1-O11 2.005(2)Å and Cu1-O21 1.984(2)Å] and a long bond [Cu1-O12 2.461(2)Å and Cu1-O22 2.371(2)Å]. This gives the

copper atom a severely distorted octahedral geometry. The bond lengths and angles are within normal ranges for a complex of this type.[77]

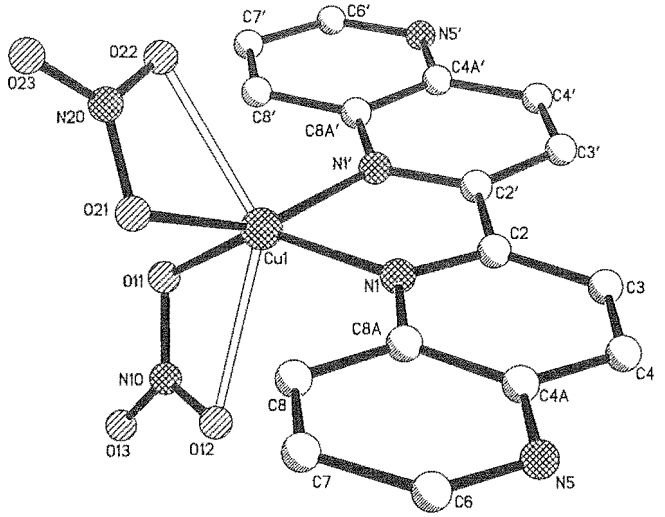


Figure 2.41 Perspective view of the asymmetric of **2.27**, with the long Cu-O bonds of the chelating nitrate anions shown as hollow. Selected bond lengths (Å) and bond angles (Å): Cu1-N1' 1.983(2), Cu1-N1 2.004(2), Cu1-O21 1.984(2), Cu1-O11 2.005(2), Cu1-O22 2.371(2), Cu1-O12 2.461(2), N1'-Cu1-O21, 152.29(10), N1'-Cu1-N1 82.40(9), O21-Cu1-N1 102.58(9), N1'-Cu1-O11 97.2(1), N1-Cu1-O11 143.45(10), N1'-Cu1-O22 96.38(9), N1-Cu1-O22 123.54(9).

The molecules arrange in ribbons of alternating mononuclear units, with the aromatic molecules coplanar and in an offset stacked arrangement. The slight offset has C4 of one ligand lying above the centre of the N1 – C8 ring, at a distance of 3.440(4)Å. The strips are attached by C-H···N interactions between the uncoordinated nitrogens of **2.5** and hydrogen atoms of adjacent molecules of **2.5**, the shortest being 2.416(6)Å between H5 and N5, as shown in figure 2.42. The complex also contains a molecule of non-coordinated acetonitrile, which occupies the spaces between the stacks of molecules.

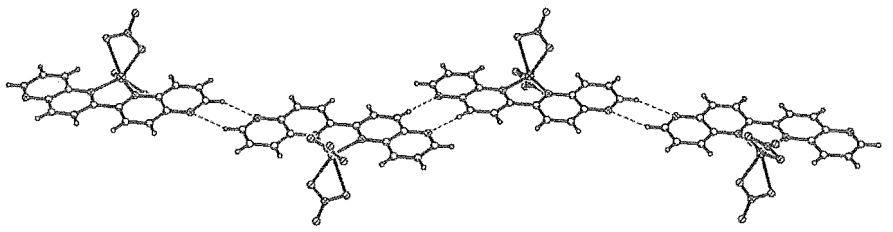


Figure 2.42 Perspective view of a hydrogen bonded ribbon of **2.27**.

2.9 Conclusion

The metallosupramolecular chemistry of a number of known *sym*-biheterocycles based on naphthalene has been investigated with a number of different metal atoms. The *sym*-biheterocycles chosen for this investigation could all bridge metal atoms in various ways. The particular binding mode observed depended on the conformation of the heterocycle, with all the ligands either *cis*-planar or *trans*-planar.

The majority of the complexes isolated were discrete, with mononuclear and dinuclear compounds isolated in most cases. The dinuclear complexes were all bridged by chloride or iodide ions. The bridging and chelating coordination sites combined in the ligand **2.3** allowed the preparation of one- and two- dimensional polymers.

The ligand **2.5** has nitrogen atoms in separate rings, forming a pyridopyridine based heterocycle, rather than a benzofused diazine. The separation of the donor atoms to different rings alleviates the steric hindrance of the nitrogen atoms. This ligand was observed to both chelate and bridge silver in the formation of a discrete M_4L_3 complex, which had ligands in two different conformations (*cis*-planar and *trans*-planar).

The isolation of mainly discrete complexes meant that secondary interactions were important in determining the three-dimensional structure. The aromatic rings of the ligands were involved in attractive face-to-face and edge-to-face interactions. Hydrogen bonding interactions were also structurally significant in a number of complexes, allowing the aggregation of simple building blocks into more complex metallosupramolecular species.

The formation of complexes from the naphthalene based multinodal *sym*-biheterocycles described above shows that these ligands are less likely to form complexes with different binding modes than are benzene based biheterocycles, such as 2,2′-bipyrazine. However, a number of discrete complexes with noncoordinating nitrogen atoms have been prepared, and these could be used in the formation of mixed-metal metallosupramolecular assemblies.

Chapter 3

Flexible Ligands

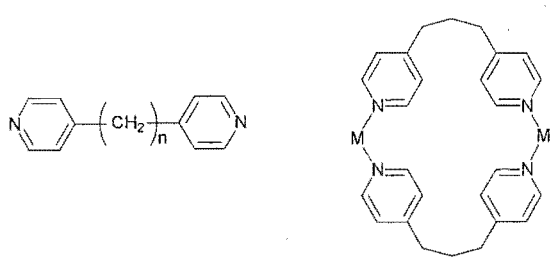
3 Flexible Ligands

3.1 Introduction

Rigid ligands constructed from N-heterocycles have been used as components in the controlled self-assembly of metallosupramolecular species for over 15 years, as outlined in chapters 1 and 2. As ligands, such molecules provide access to a limited number of possible structures, which, depending on the nature of the ligand, may be independent of the conformation of the ligand molecules.

The use of more flexible organic molecules as ligands in assemblies is a burgeoning area of interest. Such molecules provide access to topologies that are simply unavailable to their more rigid counterparts, due to the conformational freedom they possess. The flexibility is commonly introduced via linking groups constructed from combinations of methylene groups, and sulfur or oxygen atoms. The amount of flexibility that is available to the ligand depends on the number and type of flexible groups used. The topology of the coordination compounds formed from such ligands is dependent on the conformation of the ligand molecules.

The molecules used as ligands commonly rely on N-heterocycles, for reasons outlined in chapter 1, which are linked by flexible groups. A series of ligands consisting of 4-pyridyl units linked by alkyl chains of varying length (fig 3.1 (a)) shows the versatility of flexible spacer groups for the formation of different topologies. For example, spacer groups with one or two methylene groups (n=1 or 2) with cadmium nitrate allow the formation of 2-D sheets, 1-D polymers of rings[78,79] and 3-D arrays.[80] The extension of the spacer group to propylene (n=3) allows the formation of 1-D polymers of helices[81] and rings,[79,82] 2-D sheets[83] and even M_2L_2 macrocycles, shown in figure 3.1(b).[81] The further extension of the spacer group to longer alkyl chains (n = 4 – 7) allows the formation of more complicated 2-D nets and 3-D arrays, with varying degrees of interpenetration.[83,84]



(a) (b)

Figure 3.1

Flexible ligands constructed from N-heterocycles other than pyridine have also been used to form complexes with varying topologies. The use of a different heterocycle alters the properties of the ligand. The reaction of derivatives of 1,3-bis(1-pyrazolyl)propane (fig 3.2) with various metals forms discrete, as well as polymeric, species.[85,86] Other heterocycles have also been investigated, with the reaction of 1,6-bis(8-quinolinyloxy)hexane (fig 3.2) with various silver salts forming 1-D helical polymeric complexes.[87]

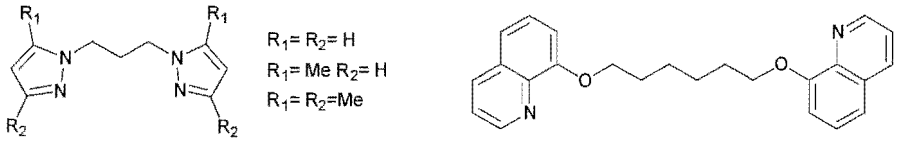


Figure 3.2

Spacer groups constructed from a combination of both flexible linking groups and rigid subcomponents is an area of increasing interest. The use of heterocyclic rings linked to aromatic groups via flexible spacer groups has been the focus of the Steel group for a number of years.[88] A stylised representation of these ligands is shown in figure 3.3. Such ligands show a propensity to form a variety of interesting structures. The possibility of varying the heterocycle, the aromatic group, the substitution pattern, the number and type of flexible spacer groups all provide a large scope for modification of the properties of any potential ligands.

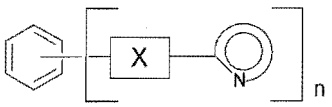


Figure 3.3

A series of ligands based on this structure, using benzene as the aromatic group, oxygen as the spacer group, and pyridine as the heterocycle have been synthesised by members of the Steel group. The use of *p*-disubstituted benzene rings has given interesting structures, with the combination of 1,4-bis(2-pyridyloxy)benzene (fig 3.4) with silver nitrate giving an M_2L_2 macrocycle, as shown by Hartshorn.[89] The isomeric ligand, 1,4-bis(3-pyridyloxy)benzene, when combined with Pd gives an intriguing quadruple helicate, as shown by McMorran.[90] This complex was found to reversibly encapsulate various complex anions, with a preference for perchlorate.[91]

Figure 3.4

Various ligands have been prepared with trisubstituted benzene rings, and diazole heterocycles, for example the isomeric molecules shown in figure 3.5. When combined with metal atoms these molecules have shown the ability to form cage-like structures. The reaction of 1,3,5-tris(1-pyrazolylmethyl)-2,4,6-triethylbenzene with palladium chloride produces an M_6L_4 cage structure,[28] while the isomeric ligand 1,3,5-tris(1-imidazolylmethyl)-2,4,6-triethylbenzene with silver perchlorate gives an M_3L_2 cage.[92] Reaction of 1,3,5-tris(1-pyrazolylmethyl)-2,4,6-trimethylbenzene with ruthenium(II) chloride showed this molecule's ability to encapsulate a metal atom. This unprecedented coordination mode involves a ruthenium atom coordinated to the benzene ring and the three pyrazole groups to give a discrete mononuclear complex which was described as a 'coelenterate'.[93]

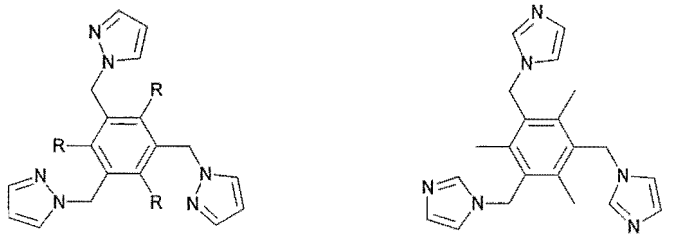


Figure 3.5

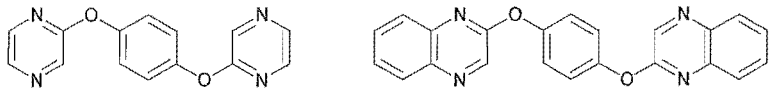
The study of coordination polymers and network solids has developed rapidly over the last 15 years.[16] The formation of different structures from the same starting components has been termed 'supramolecular isomerism'.[16] The increase in structural diversity can be divided into various categories. Structural isomerism involves the formation of different superstructures from the same starting components. The interpenetration and catenation of polymeric chains in different ways allows the formation of complexes with different properties. Isomeric polymers and networks that are enantiomeric or diastereomeric have different structures, which will respond differently to various conditions. The coordination complexes of ligands in different conformations represent a subtle form of supramolecular isomerism, which can lead to other forms of supramolecular isomerism.

Flexible ligands have been used in the formation of a variety of different coordination polymers, with the formation of numerous different structures.[94] Conformational supramolecular isomerism can be important in these structures, with the possibility that the flexible portion of a ligand may adopt different conformations in different situations. Such conformational change can give sharply differing structures, which also exhibit structural supramolecular isomerism, as has been observed in hydrogen-bonded host-guest compounds.[95] When each of the bonds between atoms of the flexible linker groups used can adopt either an *anti-* or *gauche-* conformation, these differences make significant structural changes in the complexes formed. A copper(II) nitrate complex of 1,3-bis(4-pyridinyl)propane contains ligands in different conformations, and with a mixture of *gauche-gauche* and *anti-anti*. This gives the 2-D network a rectangular appearance.[96] The isolation of different complexes containing the same ligand with different conformations is more problematic. The cobalt(II) nitrate complexes of 1,3-bis(4-pyridinyl)ethane with different solvate molecules give isomeric complexes, differing in the conformation of the flexible ligand.[97]

This chapter will investigate the structural metallosupramolecular chemistry of complexes from flexible ligands of the general structure shown in figure 3.3. As outlined above, the flexibility inherent in these ligands allows their complexes to have novel topologies.

3.2 Pyrazine and Quinoxaline –O– spaced

The combination of N-heterocycles to give so-called 'multinodal' ligands has been discussed in chapter 2. The combination of the two flexible ligands shown in figure 3.4 can be envisaged in the potential ligand **3.1**, shown in figure 3.6. The use of heterocycles with multiple donor sites as part of flexible ligands is a largely unexplored area. An exception to this is the investigations of the coordination chemistry of flexible ligands involving pyrazine heterocycles. These show that when reacted with copper(I) and silver the pyrazine moiety can either bridge two metal atoms,[98,99] or coordinate through one nitrogen only.[100,101] The ligands **3.1** and **3.2** were synthesised to investigate the coordination chemistry of these potentially flexible 'multinodal' ligands.

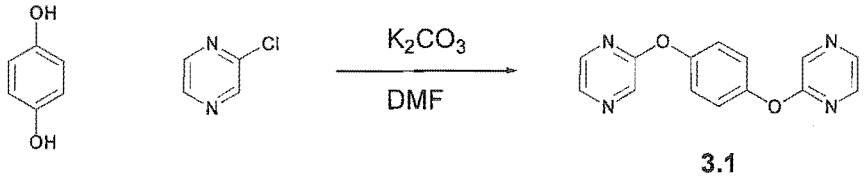


3.1 3.2

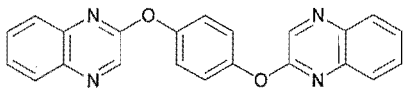
Figure 3.6

3.2.1 Ligand Synthesis

The ligands 1,4-bis(2-pyrazinyloxy)benzene (**3.1**) and 1,4-bis(2-quinoxalinyl oxy)benzene (**3.2**) were synthesised in an extension of the method of O'Keefe,[102] by nucleophilic substitution of two equivalents of 2-chloroheterocycle by hydroquinone, in warm N,N-dimethylformamide in the presence of potassium carbonate (scheme 3.1). The precursor to **3.2**, 2-chloroquinoxaline, was prepared from 2-hydroxyquinoxaline using the method of Gowenlock et al.[103] The new ligands, **3.1** and **3.2**, were produced in modest (44%) and good (68%) yields, respectively, as white solids.



3.1



3.2

Scheme 3.1

3.2.2 Coordination complexes of 3.1 and 3.2

The coordination chemistry of **3.1** and **3.2** was investigated by the formation of complexes with $AgNO_3$, $PdCl_2$, $Cu(NO_3)_2$, CuI, and $Cd(NO_3)_2$. The reaction of **3.1** and **3.2** with $AgNO_3$ produced the silver nitrate complexes, **3.3** and **3.4**, respectively, as brown solids. These solids both analysed with 1:1 metal to ligand-stoichiometry, and were insoluble in common solvents. Despite numerous efforts, no crystals of **3.3** or **3.4** could be isolated. The analysis results and general insolubility might indicate that the complexes are polymeric.

The reactions of **3.1** and **3.2** with Li_2PdCl_4 in methanol gave the complexes **3.5** and **3.6**, respectively. Complex **3.5** was only isolated as a black precipitate that could not be

identified. Complex **3.6** was isolated as a yellow solid which analysed with a 1:1 metal-ligand stoichiometry. This complex was insoluble in common NMR solvents. No further analysis was attempted.

The copper complexes, **3.7** and **3.8**, were prepared by reacting **3.1** and **3.2** with copper(II) nitrate in methanol. These blue complexes analysed with 1:3 and 1:1 metal-ligand stoichiometries, respectively. These complexes were insoluble in common solvents, possibly suggesting polymeric structures. No further analysis was undertaken.

The reaction of **3.1** and **3.2** with copper(I) iodide in acetonitrile produced the complexes, **3.9** and **3.10**, respectively. These both analysed as $[Cu_2I_2.\mathbf{L}]$. Single crystals suitable for X-ray structure analysis were isolated by carefully layering an acetonitrile solution of CuI onto an acetonitrile solution of ligand.

The cadmium chloride complexes, **3.11** and **3.12**, were isolated as colourless precipitates. The complexes analysed as $[(CdCl_2)_2.(\mathbf{3.1}).2½H_2O]$ and $[CdCl_2.(\mathbf{3.2}).½H_2O]$, respectively. The complexes were both soluble only in DMSO, and an NMR analysis showed only noncoordinated ligand. The stoichiometry and general insolubility could indicate polymeric structures for **3.11** and **3.12**.

Crystal structure of **3.9**

The copper(I) iodide complex, **3.9**, has a polymeric structure. The complex crystallizes in the triclinic space group P-1, with half the ligand (**3.1**) and a copper(I) iodide in the asymmetric unit. The ligand lies on a centre of inversion, which is at the centroid of the aryl ring, and bridges two copper atoms at a distance of 15.821(4)Å, as shown in figure 3.7. The pyrazine rings of the ligand are inclined at an angle of 74.5(2)° to the benzene ring, and coordinate the copper atoms through the less hindered nitrogen atoms, with a Cu-N bond distance of 2.062(2)Å. The copper atom is also coordinated by three iodine atoms with Cu-I bond lengths between 2.6310(8)Å and 2.6804(8)Å, and has a slightly distorted tetrahedral geometry (largest distortion 117.22(1)°).

The structure of **3.9** extends through a ribbon of copper(I) iodide units, as shown in figure 3.8. The polymer consists of fused Cu_2I_2 rings that lie with a centre of inversion at the centroid. The geometry of the iodine is distorted T-shaped, which, combined with the tetrahedral geometry of the copper, give the ring a rhomboid shape. The polymer consists of two rhomboids which have similar geometry and size, with distances between the copper atoms of 2.779(2)Å and 2.795(2)Å. Cu_2I_2 rhomboids are tilted at an angle of 33.5(1)° to one another, and this gives the polymer a so-called 'staircase' motif.[104] The

copper(I) iodide ribbons propagate down the *a*-axis and are bridged by the ligand molecules, giving a sheet structure. The stacked ligands of the sheets are related by translation and therefore the aromatic rings of stacked molecules are coplanar. However, the rings do not overlap as is necessary for any π-π interactions to occur.

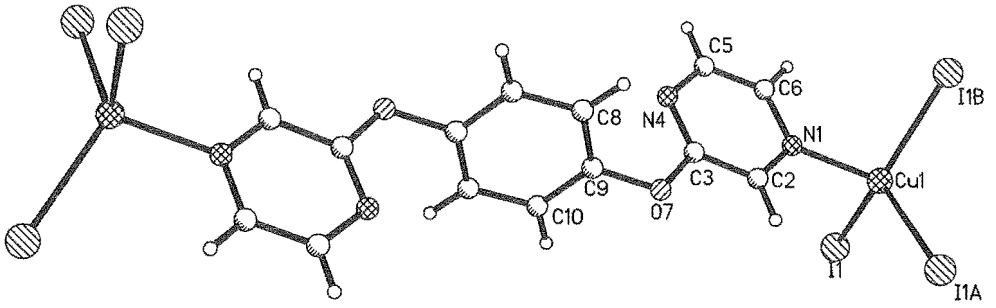


Figure 3.7 Perspective view of the structure of **3.9**, showing the atomic labelling. Selected bond lengths (Å) and angles (°): Cu1-N1 2.062(2), Cu1-I1A 2.6310(8), Cu1-I1B 2.6545(9), Cu1-I1 2.6804(8), N1-Cu1-I1A 110.06(7), N1-Cu1-I1B 104.08(8), N1-Cu1-I1 101.89(7), I1A-Cu1-I1B 116.16(2), I1A-Cu1-I1 106.36(3), I1B-Cu1-I1 117.22(2).

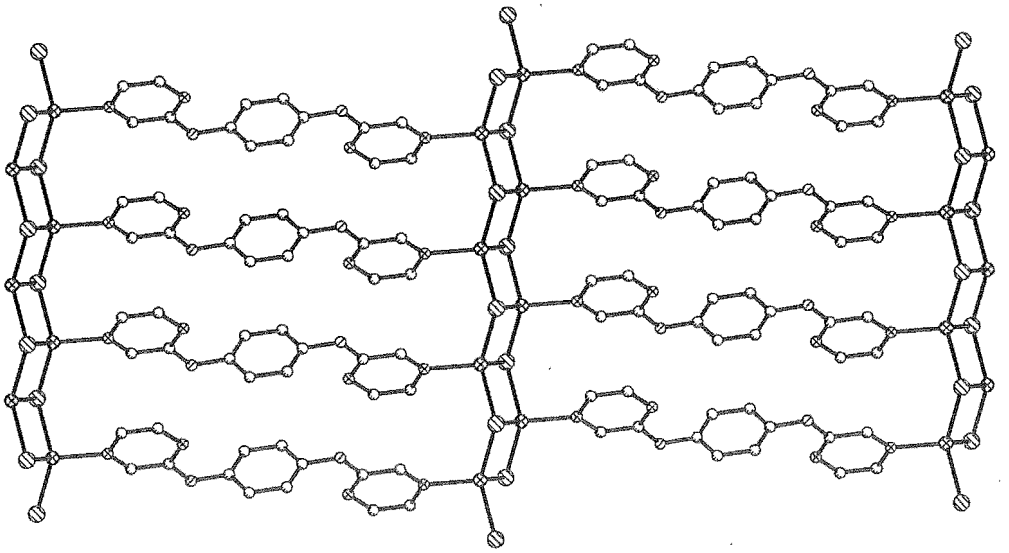


Figure 3.8 View of the sheet structure of **3.9**, with the copper(I) iodide ribbons shown. The hydrogen atoms have been omitted for clarity.

Crystal Structure of **3.10**

The structure of **3.10** is also a two-dimensional sheet polymer, similar to that of **3.10**. The complex exists in the monoclinic space group $P2_1/n$, with half a molecule of **3.2** and one copper(I) iodide in the asymmetric unit. Similar to the structure of **3.9** above, the ligand molecule lies with a centre of inversion at the centroid of the benzene ring. The ligand bridges two copper atoms at a distance of 15.745(4)Å, as shown in figure 3.9. The quinoxaline rings of **3.2** are planar (mean deviation 0.023(4)Å), and inclined at an angle of 64.3(1)° to the benzene ring. The ligand coordinates the copper through the less hindered nitrogen, with a Cu1-N1 bond distance of 2.051(4)Å. The copper atom is also bound to three iodine atoms with Cu-I bond lengths between 2.625(2) and 2.705(2)Å, and has a distorted tetrahedral geometry, similar to that of **3.10** above (largest distortion 119.73(4)°).

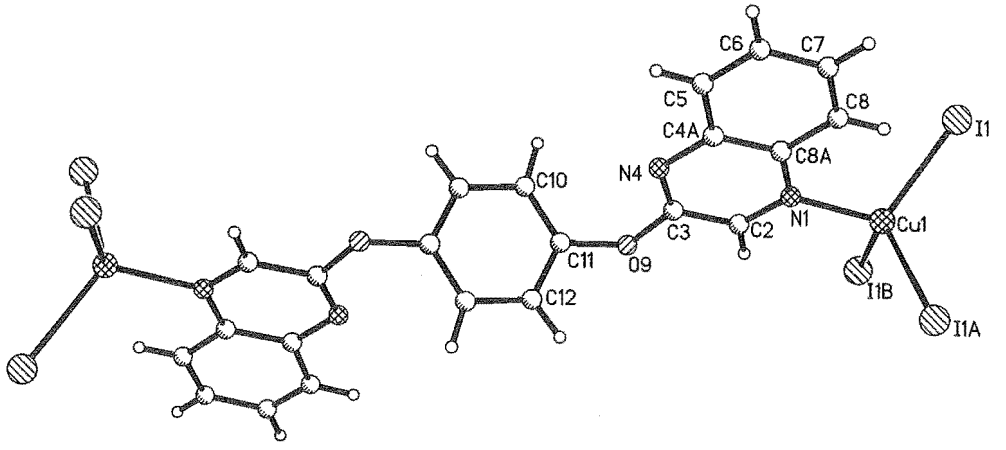


Figure 3.9 Perspective view of **3.10**, showing a molecule of **3.2** and atomic labelling. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.051(4), Cu1-I1A 2.625(2), Cu1-I1 2.652(2), Cu1-I1B 2.705(2), N1-Cu1-I1A 107.3(1), N1-Cu1-I1 114.6(1), I1A-Cu1-I1 119.73(4), N1-Cu1-I1B 106.8(1), I1A-Cu1-I1B 106.25(7), I1-Cu1-I1B 100.94(4).

As in **3.9** above, the structure of **3.10** extends through a ribbon of polymeric copper(I) iodide units, as shown in figure 3.10. The polymeric ribbon consists of Cu_2I_2 rings, which surround a centre of inversion. The Cu_2L_2 units have a rhomboid shape and are fused, with an angle between the units of 64.0(1)°, giving a polymeric 'staircase' motif similar to **3.9** above. However, unlike **3.9**, the rhomboid units of **3.10** are different, with oblique angles of 119.7(1)° and 100.9(1)°. This leads to Cu···Cu distances of 2.650(3)Å and 3.410(3)Å, respectively.

The copper(I) iodide ribbons propagate down the *a*-axis, and are bridged by ligands on alternating sides. The aromatic rings of the stacked ligands are coplanar with the quinoxaline rings overlapping in such a way that the fused benzene ring of one overlaps the fused pyrazine of another, 3.375(3)Å apart. This structure is similar to that formed by the reaction of copper(I) bromide with quinoxaline.[105] However, in this case the quinoxaline rings bridge the copper atoms through both ring nitrogens, leading to a structure in which the copper halide ribbons are much closer together.

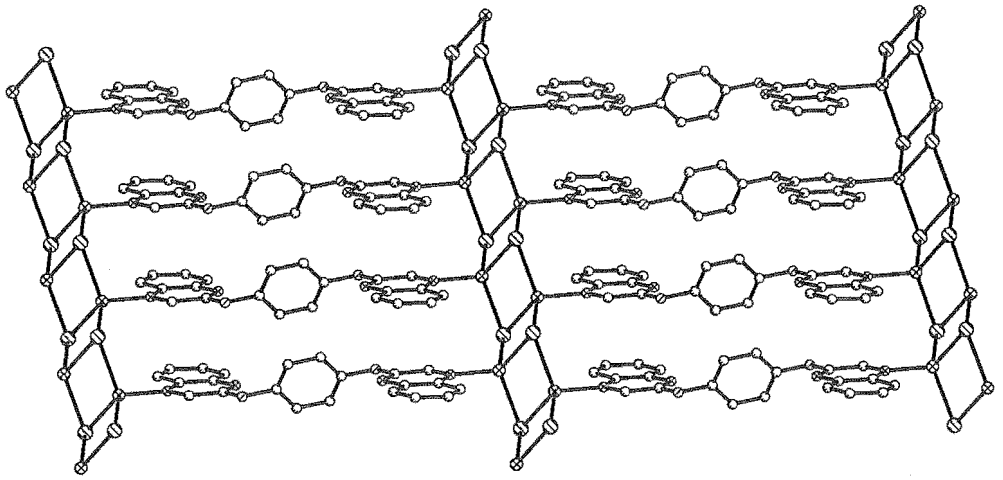


Figure 3.10 View of the sheet structure of **3.10**, with the copper(I) iodide ribbons and π-π stacked quinoxaline rings shown. The hydrogen atoms have been removed for clarity.

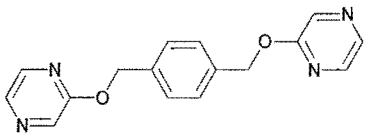
A comparison of the structures of the complexes of CuI with ligands **3.1** and **3.2** shows that a subtle change in the ligand can have interesting effects on the structures formed. The structures are quite similar, with the same overall two-dimensional sheet topology of polymeric CuI 'staircase' pillars bridged by ligands. Both the ligands are situated on centres of inversion at the centroid of the central benzene ring, and coordinate the copper through the less hindered nitrogen atom. The structures differ in the ability of the heterocycle to be involved in π-π face-to-face interactions. The qunioxaline ring system has a larger area which can be involved in such interactions, while the pyrazine ring is smaller. This requires that the ligands have a slightly different conformation, which leads to small differences in the overall structures.

These structures represent two of only five examples of CuI 'staircase' structures where the bridging ligands are nitrogen-containing heterocycles. The other structures also involve diazine based ligands, with 2,2′-dimethyl-4,4′-bipyrimidine,[42] 2-

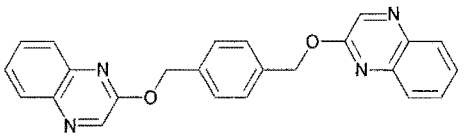
methylpyrazine[106] and quinoxaline[105] being the other examples. The structures **3.9** and **3.10** represent the only examples of complexes of this type which involve 'flexible' bridging ligands.

3.3 Pyrazine and Quinoxaline $-CH_2O-$ spaced

The two structurally characterised complexes of flexible ligands **3.1** and **3.2** only coordinated metal atoms through the less hindered nitrogen atoms. The noncoordinated nitrogen atoms have a more sterically hindered environment due to the proximity of the bridging hydroquinone group. Interestingly, the inability of these donors to coordinate is in marked contrast to the work of Hartshorn, which showed that coordination of metals by 2-substituted pyridine groups with bridging hydroquinone groups was possible.[107] This could be due to the fact that pyrazine is less basic than pyridine, and therefore forms weaker coordination bonds with metal atoms. It was decided to investigate the coordination chemistry of the ligands **3.13** and **3.14** (fig 3.11), which differ from **3.1** and **3.2** by the extension of each spacer group by a methylene group. The longer spacer increases the distance between the benzene and the heterocycles, and should lower the steric hindrance of the adjacent nitrogen atoms.



3.13

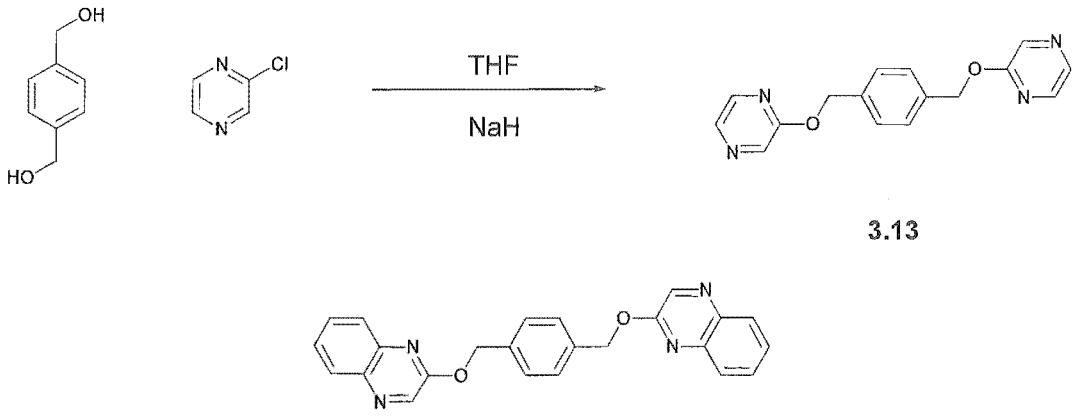


3.14

Figure 3.11

3.3.1 Ligand Synthesis

The new ligands 1,4-bis(2-pyrazinyloxymethyl)benzene (**3.13**) and 1,4-bis(2-quinoxalinyloxymethyl)benzene (**3.14**) were synthesised by reacting two equivalents of 2-chloroheterocycle with 1,4-benzenedimethanol in refluxing THF, in the presence of sodium hydride (scheme 3.2). The ligands, **3.13** and **3.14**, were isolated in 75% and 73% yields, respectively, and characterised by NMR spectroscopy, mass spectrometry and elemental analysis.



3.13

3.14

Scheme 3.2

3.3.2 Coordination complexes of 3.13 and 3.14

The coordination complexes of **3.13** and **3.14** with $AgNO_3$, $PdCl_2$, $Cu(NO_3)_2$, CuI and $CdCl_2$ were prepared. The reactions of **3.13** and **3.14** with silver nitrate gave the complexes **3.15** and **3.16** as off-white and brown solids, respectively; both complexes analysed with a 1:1 metal-ligand stoichiometry. The brown complex, **3.16**, proved to be insoluble in common solvents, and attempts to form single crystals suitable for X-ray structure analysis were not successful. No further analysis was undertaken. The off-white complex, **3.15**, was more soluble, and X-ray quality crystals were grown by diffusion of ether into a nitromethane solution of **3.15**.

The reactions of **3.13** and **3.14** with Li_2PdCl_4 in a 1:1 acetone-methanol gave the complexes **3.17** and **3.18**, respectively. Complex **3.17** could only be isolated as a black precipitate that could not be identified. Complex **3.18** was isolated as a yellow solid which analysed with a 2:1 metal-ligand stoichiometry. This complex was insoluble in common NMR solvents. The insolubility and analysis results suggest that these complexes might be polymeric. No further analysis was attempted.

The reactions of **3.13** and **3.14** with copper(II) chloride in methanol gave the complexes **3.19** and **3.20**, respectively. These blue solids were insoluble in common solvents, and analysed with 3:2 and 2:1 metal-ligand stoichiometries, respectively. Despite these possibly interesting stoichiometries, no X-ray quality crystals could be grown. No further analysis was undertaken.

The copper(I) iodide complexes of **3.13** and **3.14** were prepared by reaction of the ligands with CuI in 1:1 acetone-acetonitrile solution, giving the yellow complexes **3.21** and **3.22**, respectively. Both complexes were insoluble in common solvents and had a 1:2

metal-ligand stoichiometry, possibly indicating the complexes are polymeric. Due to the interesting structures produced by the structurally related ligands **3.1** and **3.2**, numerous attempts to form crystals suitable for X-ray structure analysis were attempted. However, none of the approaches used were successful, and no further analysis was undertaken.

The reactions of **3.13** and **3.14** with $CdCl_2$ in methanol gave the cadmium chloride complexes, **3.23** and **3.24**, respectively. The complexes both analysed with 1:1 metal-ligand stoichiometry, and were insoluble in common solvents
stoichiometry could be indicative of the formation of polymeric

Crystal structure of **3.15**

The silver nitrate complex, **3.15**, crystallizes in the mon
half a molecule of **3.13** and half a silver nitrate in the asy
3.15, shown in figure 3.12, is a one-dimensional polymeric.
that the nitrate counterion was significantly disordered. H
the silver atom, and a description of the structure is possibl

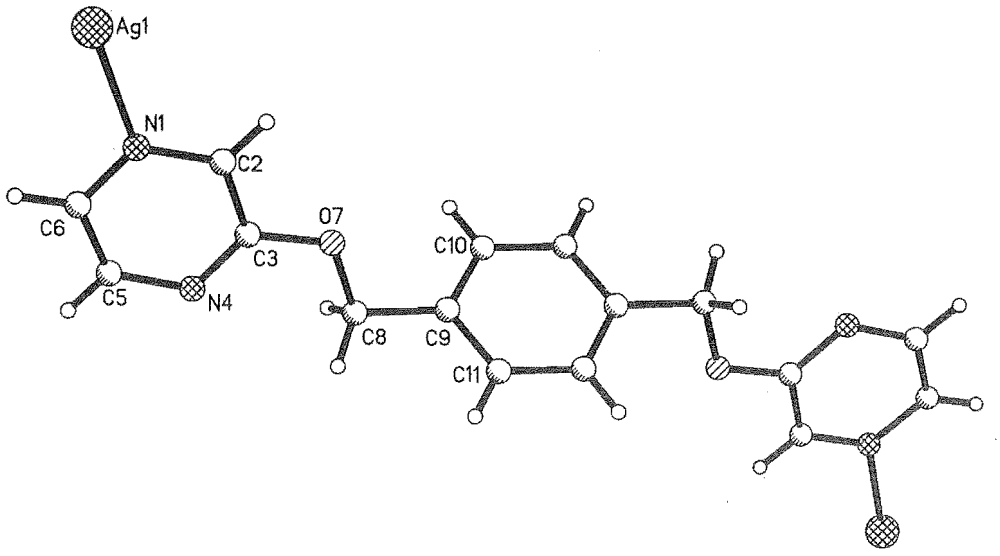


Figure 3.12 Perspective view of the structure of **3.15**, with atomic labelling shown. The disordered nitrate counterion has been removed for clarity. Selected bond length (Å): Ag1-N1 2.163(3).

The ligand, **3.13**, has a centre of inversion at the centroid of the benzene ring, and bridges two silver atoms through the less hindered nitrogen. The pyrazine rings of the ligand molecule are planar and inclined to that of the benzene ring at an angle of 64(1)°. The silver atom also lies on a centre of inversion, and is coordinated by two ligand nitrogen atoms, with an Ag-N bond length of 2.161(3)Å. The silver atoms of the polymer are 17.554(2)Å apart.

The polymers chains of **3.15** arrange with the silver atoms stacked in columns, 3.556(2)Å apart. The columns assemble with large cavities between the stacks, shown in figure 3.13, which contain disordered nitrate counterions. The pyrazine rings of the ligand, **3.13**, are overlapped, with the meanplanes in an offset stacked alignment, indicating a π-π face-to-face interaction between the rings.

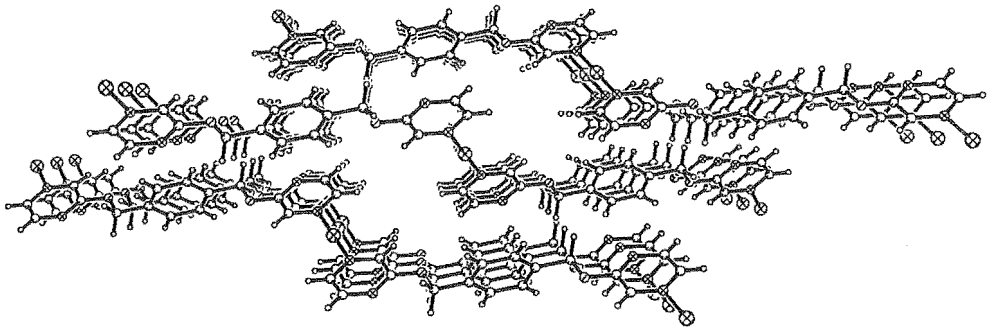


Figure 3.13 Perspective view of the packing of **3.15** down the *b*-axis; disordered counterions have been omitted for clarity.

The structural characterisation of this complex, combined with that of copper(I) iodide complexes of **3.1** and **3.2** shows that, in these cases, the pyrazine and quinoxaline heterocyclic groups coordinate through the less hindered nitrogen atoms preferentially. The increase of the length of the spacer group in an attempt to from complexes involving the more hindered nitrogen atoms was unsuccessful. The complexes structurally characterised above exemplify the ability of these ligands to form polymeric compounds. This result is not unexpected, as the less hindered nitrogen atoms of these ligands are oriented away from one another. However, it is interesting that the increase in flexibility seems to have little effect.

3.4 Hydroquinone based $-CH_2O-$ ligands

The extension of 1,4-bis(2-pyridyloxy)benzene (fig 3.4) to include spacer groups containing two atoms was also attempted by Hartshorn using the two molecules shown in figure 3.14. These isomeric molecules differ only in the order of the atoms in the spacer groups. The coordination chemistry of these molecules was investigated by the formation of various complexes, with 1-D polymeric complexes involving silver nitrate, and a discrete M_2L_2 macrocycle involving 1,4-bis(2-pyridylmethoxy)benzene and palladium chloride, which were structurally characterised by X-ray crystallography.[108]

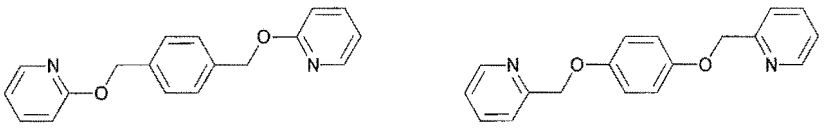
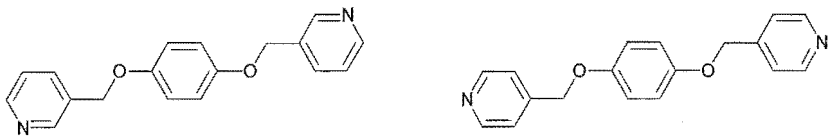


Figure 3.14

The coordination of the ligands **3.1**, **3.2** and **3.13** through only the less hindered nitrogen atoms in the complexes above led us to investigate the coordination chemistry of 1,4-bis(3-pyridyloxymethyl)benzene (**3.25**) (fig 3.15). This molecule is similar to the pyrazine containing molecule **3.13**, with the more hindered nitrogen atoms replaced by CH groups. It represents an extension of the ligand 1,4-bis(3-pyridyloxy)benzene (fig 3.4), which was used by McMorran to form quadruple helicates with palladium. The extension of the spacer group could allow the potential ligands formed to exhibit different conformations to those of flexible ligands involving single atom spacer groups, due to the increase in conformational freedom within these spacer groups.



3.25 **3.26**

Figure 3.15

The isomeric ligand 1,4-bis(4-pyridylmethyloxy)benzene (**3.26**) (fig 3.15) was also synthesised. This represents an extension of linear flexible molecules such as 1,4-bis(4-pyridylmethyl)benzene, which is flexible enough to form an M_2L_2 macrocycle with $M(en)(NO_3)_2$, where M = Pd or Pt, as shown in figure 3.16. This ligand, also forms

polymeric 'ladder' complexes with cadmium salts, exemplifying the versatility of this flexible ligand.[109]

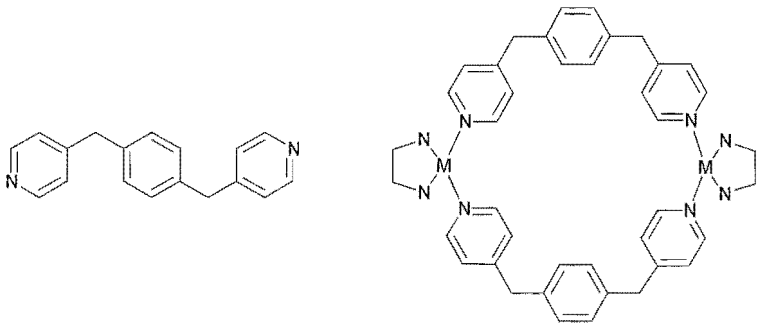
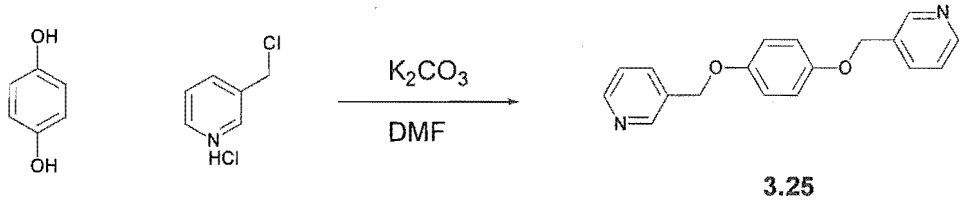


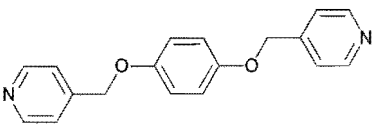
Figure 3.16

3.4.1 Ligand Synthesis

The ligands, 1,4-bis(3-pyridylmethoxy)benzene (**3.25**) and 1,4-bis(4-pyridylmethoxy)benzene (**3.26**), were synthesised by a further extension of the methods used above. Nucleophilic substitution of two equivalents of 3-chloromethylpyridine and 4-chloromethylpyridine by hydroquinone in warm N,N-dimethylformamide, in the presence of potassium carbonate, gave **3.25** and **3.26** in 39% and 63% yields, respectively (scheme 3.3). The ligands were purified by column chromatography and crystallization, and characterised by NMR spectroscopy, mass spectrometry and elemental analysis.



3.25



3.26

Scheme 3.3

3.4.2 Coordination complexes of 3.25

The coordination chemistry of **3.25** was investigated by formation of complexes with $AgNO_3$ (**3.27**), $PdCl_2$ (**3.28**), $Cu(NO_3)_2$ (**3.29**), CuI (**3.30**), $Cu(PPh_3)_2NO_3$ (**3.31**), $Cd(NO_3)_2$ (**3.32**) and $ZnBr_2$ (**3.33**). The reaction of **3.5** with silver nitrate gave a white crystalline

solid, **3.27**, which analysed as [$AgNO_3$.(**3.25**).½H_2O]. Single crystals suitable for X-ray structure analysis were grown from the slow evaporation of an acetonitrile solution of **3.27**.

The reaction of **3.25** with a solution of Li_2PdCl_4 in methanol gave a yellow powder, **3.28**, which analysed with a 1:1 metal-ligand stoichiometry. The complex proved to be extremely insoluble, and this, coupled with the 1:1 metal-ligand stoichiometry, indicates that the structure of **3.28** might be polymeric. No further analysis was carried out.

The reaction of **3.25** with copper(II) nitrate gave **3.29** as a blue crystalline solid, which analysed as [$(Cu(NO_3)_2)_2$.(**3.25**).H_2O]. Single crystals suitable for X-ray structure analysis were grown by layering a methanol solution of $Cu(NO_3)_2$ onto a dichloromethane solution of **3.25**.

The copper(I) iodide complex, **3.30**, was isolated as a white crystalline solid, which analysed as [Cu_2I_2.(**3.25**)]. This complex was insoluble in common solvents. Despite numerous attempts, no crystals were grown of this complex.

A copper(I) bistriphenylphosphine nitrate complex, **3.31**, was isolated from the reaction of $Cu(PPh_3)_2NO_3$ with **3.25** in methanol. This complex analysed as [$(Cu(PPh_3)_2NO_3)_2$.(**3.25**)], and an NMR spectrum of the complex in acetonitrile showed only noncoordinated ligand. The complex was also analysed using electrospray mass spectrometry, which showed a range of species, including $[CuL]^+$ and $[Cu(PPh_3)L]^+$, but could not be used to definitively assign the structure. The complex was isolated from a methanol solution of **3.31** as crystals suitable for X-ray crystal structure analysis.

The reaction of **3.25** with cadmium nitrate gave a white crystalline solid, **3.32**, which analysed with an 1:1 stoichiometry. This complex was soluble in coordinating solvents, such as acetonitrile, and an NMR spectrum showed only noncoordinated ligand. Single crystals suitable for X-ray structure analysis were isolated by slow evaporation of the mother liquor solution.

Layering a solution of zinc bromide in methanol onto a solution of **3.25** in dichloromethane gave **3.33** as white crystals. These crystals analysed as [$ZnBr_2$.(**3.25**)] and were suitable for single crystal structure analysis.

Crystal structure of 3.27

The silver nitrate complex, **3.27**, has a one-dimensional polymeric structure, shown in figure 3.17, which crystallizes in the triclinic space group P-1. The complex crystallizes with two independent half-molecules of **3.25**, a silver nitrate, and a water solvate molecule in the asymmetric unit. The different ligand molecules each reside with the centroid of the

benzene ring on a crystallographic centre of inversion. The different ligand groups have similar conformations with the pyridine groups inclined to the benzene rings at angles of 70.4(1)° and 70.2(1)°. The different pyridine groups are almost coplanar with the meanplanes at an angle of 2.3(1)°. The silver atom has a slightly distorted linear coordination geometry [176.7(1)°], with Ag-N bond lengths of 2.134(3)Å and 2.137(3)Å.

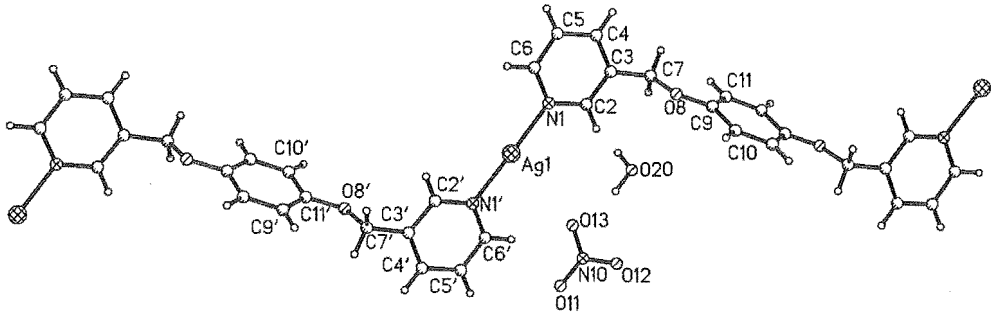


Figure 3.17 Perspective view of the structure of **3.27**, with the asymmetric unit labelled. Selected bond lengths (Å) and bond angles (°): Ag1-N1' 2.134(3), Ag1-N1 2.137(3), N1'-Ag1-N1 176.71(9).

The polymeric chains of **3.27** stack down the *a*-axis of the unit cell, as shown in figure 3.18, with the silver atoms arranged in columns 5.465(2)Å apart, the length of the *a*-unit cell edge. The polymeric chains of adjacent stacks interact, with the edge of one of the benzenes oriented towards the face of a pyrazine ring. The closest interaction (2.76(8)Å) is between H11 and the centre of the C5-C6 bond.

The columns arrange with large cavities between the layers, similar to the structure of **3.15** above. In the structure of **3.15** the nitrate counterions occupy the cavities and are disordered. In the structure of **3.27** the nitrate counterions share the cavities with solvate water molecules and are not disordered. The solvate water molecules are hydrogen bonded to the oxygens of the nitrate counterions, with D values, O20A···O13 2.849(4)Å and O20B···O12 2.861(5)Å, and θ values of 166(4)° and 174(5)°, respectively. These correspond to moderately strong hydrogen bonds,[4] and these interactions may explain why the nitrate counterion is not disordered in this structure.

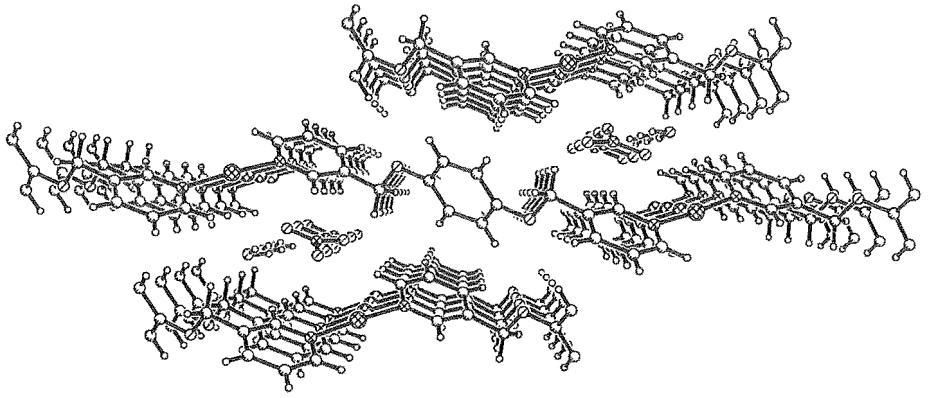


Figure 3.18 Perspective view of the packing of **3.27** looking down the *a*-axis of the unit cell. The water molecules and nitrate counterions are shown in the cavities between the polymeric chains.

Crystal structure of **3.29**

The copper(II) nitrate complex, **3.29**, crystallizes in the monoclinic space group $P2_1/n$, with one molecule of **3.25** and half of a copper(II) nitrate in the asymmetric unit. The complex has a 'necklace' structure, which is a one-dimensional polymer made up of macrocyclic units, as shown in figure 3.19. Each copper atom is coordinated to four

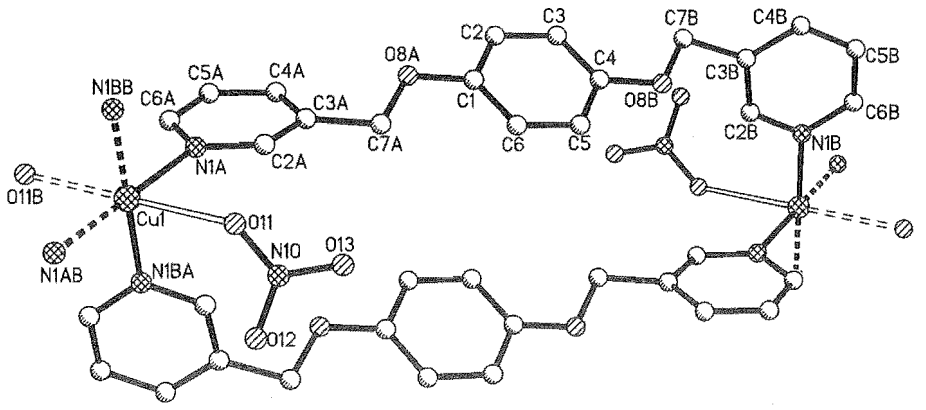


Figure 3.19 Perspective view of one of the macrocyclic units of the polymeric structure of **3.29**, with the longer Cu-O bonds shown as hollow. The hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1BA 2.000(2), Cu1-N1A 2.059(2), Cu1-O11 2.507(2), N1B-Cu1-N1 90.42(10), N1A-Cu1-O11 93.05(9), N1B-Cu1-O11 93.90(8).

nitrogen atoms, from four molecules of **3.25**, and two oxygen atoms of nitrate anions. The copper atom lies on a centre of inversion, and has Cu-N bond lengths of 2.000(2)Å and 2.059(2)Å, and a Cu-O bond length of 2.507(2)Å. The copper atom has an octahedral coordination geometry, with the longer Cu-O bond length reflecting Jahn-Teller distortions.[110]

The coordinated pyridines of the 30-membered M_2L_2 macrocycle are in a *cis*-relationship on the copper atom, with the distance between the two copper atoms within the macrocycles being 16.163(1)Å. The pyridine rings of the ligand are inclined at an angle of 84.4(1)° to one another, and are inclined at angles of 27.5(1)° and 71.2(1)° to the benzene ring. The *cis*-relationship of the pyridines leads to a conformation of the ligand in which there is no π-π stacking between the aromatic rings of the macrocycle, unlike in other structures of related ligands.

The copper atoms of the 'necklace' polymer stack down the *a*-axis of the unit cell, as shown in figure 3.20. The distance between the copper atoms in this stack is 8.437(1)Å, the length of the *a*-unit cell edge. The polymers propagate along the *ac*-diagonal of the unit cell, with this distance being identical to the distance between the copper atoms of the polymer. The polymer chains arrange with the nitrate counterions of one polymer adjacent to the benzene group of another. This allows C-H···O interactions with the hydrogen atoms of benzene and pyridine rings. These interactions, with H···O distances of 2.317(4)Å and 2.617(4)Å, are the only significant interactions between adjacent stacks of polymeric strands.

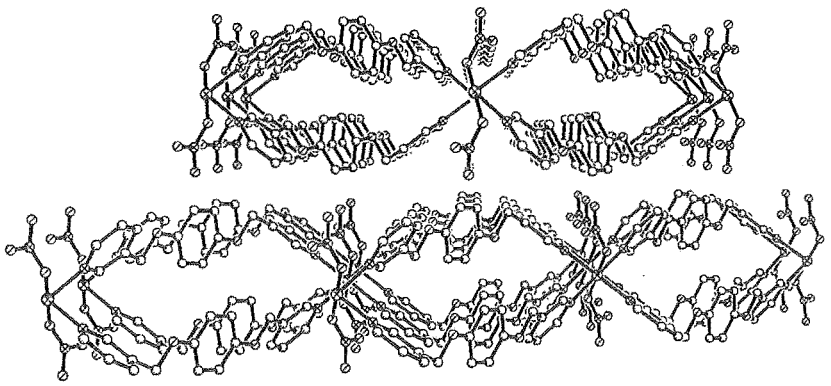


Figure 3.20 Perspective view of the packing of **3.29** looking down the *a*-axis of the unit cell, showing the columns of copper atoms. The hydrogen atoms have been omitted for clarity.

The conformation of the bridging ligand means that the macrocycles of **3.29** do not surround a cavity. As a consequence of this, there can be no interpenetration of the polymeric strands by the macrocycle. Furthermore, the lack of a cavity means that the structure cannot encapsulate anions or solvate molecules. This has interesting consequences for the formation of encapsulating and interpenetrating complexes from flexible ligands.

Crystal structure of **3.31**

Unlike the polymeric structures above containing the ligand **3.25**, the complex **3.31** has a discrete dinuclear structure, in which the ligand bridges two copper atoms, as shown in figure 3.21. The complex crystallizes in the centrosymmetric triclinic space group P-1, with the centroid of the benzene ring of the ligand lying on a centre of inversion. The pyridine groups of the ligand are inclined to the benzene ring at an angle of 93.0(1)°. As a consequence the ligand forms a linear bridge between the copper atoms, which are held

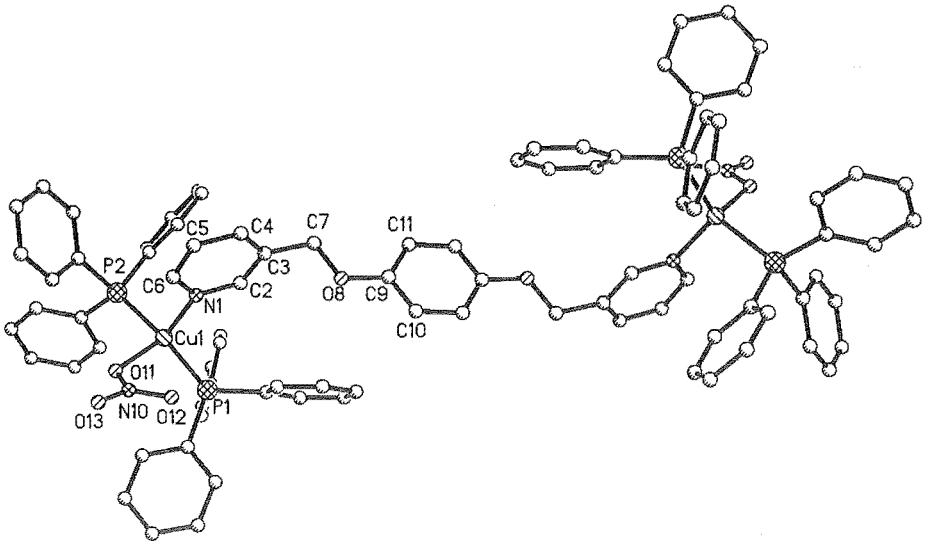


Figure 3.21 Perspective view of the structure of **3.31**, with selected atomic labelling; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.061(2), Cu1-O11 2.160(1), Cu1-P1 2.2504(7), Cu1-P2 2.2810(6), N1-Cu1-O11 98.83(6), N1-Cu1-P1 115.73(4), O11-Cu1-P1 107.98(4), N1-Cu1-P2 104.07(4), O11-Cu1-P2 100.31(4), P1-Cu1-P2 125.68(2).

16.686(2)Å apart. The copper atom is coordinated by one pyridine nitrogen, one nitrate oxygen and two triphenylphosphine phosphorus atoms, with bond lengths of Cu1-N1 2.061(2)Å and Cu1-O11 2.160(1)Å. The copper atom has a distorted tetrahedral geometry, which is caused by the steric bulk of the large triphenylphosphine groups. The sterically hindered nature of the copper atom might also explain why this structure is discrete, with the copper atom coordinated by the smaller nitrate anion, rather than the pyridine of another bridging ligand molecule.

The triphenylphosphine groups of **3.31** are both involved in 'hexa-aryl embrace' type interactions.[71] These interactions, outlined in chapter 2, involve two triphenylphosphine groups in which the aryl groups are interleaved, and between which six edge-to-face interactions occur. The triphenylphosphine groups are both related to triphenylphosphine groups of other molecules by centres of inversion. The groups are quite close, with the phosphorus atoms 6.564(2)Å and 6.732(2)Å apart, and almost colinear, with angles of 172.9(1)° and 176.5(1)°. The closest approach of these aryl groups in the 'hexa-aryl embrace' occurs between a hydrogen *ortho* to the P-C bond and the plane of another ring. These interactions occur in the range 2.562(4) – 2.974(4)Å for the two 'hexa-aryl embrace' interactions.

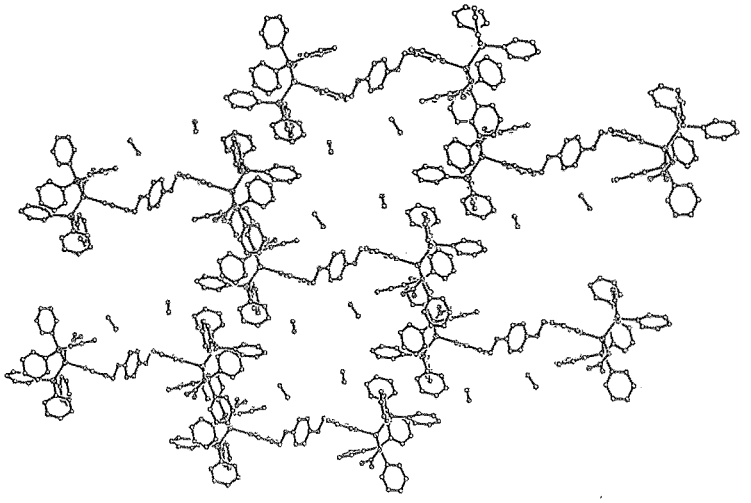


Figure 3.22 Perspective view of one layer of the pseudo polymeric sheet of **3.31**, showing the columns of 'hexa-aryl embrace' interactions and solvate containing cavities. The hydrogen atoms have been omitted for clarity.

The dinuclear copper units of **3.31** arrange into columns with alternating ligands interacting via a 'hexa-aryl embrace'. The columns are bridged by ligand molecules to form a pseudo two-dimensional polymeric sheet, as shown in figure 3.22. The space between the alternating ligand molecules is occupied by methanol solvate molecules. The layers arrange slightly offset so that the solvate containing cavities are closed, which traps the solvent inside. The solvate molecules are hydrogen bonded to the noncoordinated oxygen atoms of nitrate groups from the offset layers, with D values of 2.916(3)Å and 2.932(3)Å, and θ values of 161.4(1)° and 165.8(1)°, respectively (see chapter 2).

Crystal structure of **3.32**

The structure of the $Cd(NO_3)_2$ complex, **3.32**, is remarkably similar to that of the $Cu(NO_3)_2$ complex, **3.29**. The complex crystallizes in the same space group, $P2_1/n$, with the largest deviation in cell lengths being only 0.6Å for the *c*-axis. As in structure **3.29**, the complex has a 'necklace' structure, which is a one-dimensional polymer made up spiro-macrocyclic units, as shown in figure 3.23. The cadmium atom lies on a centre of

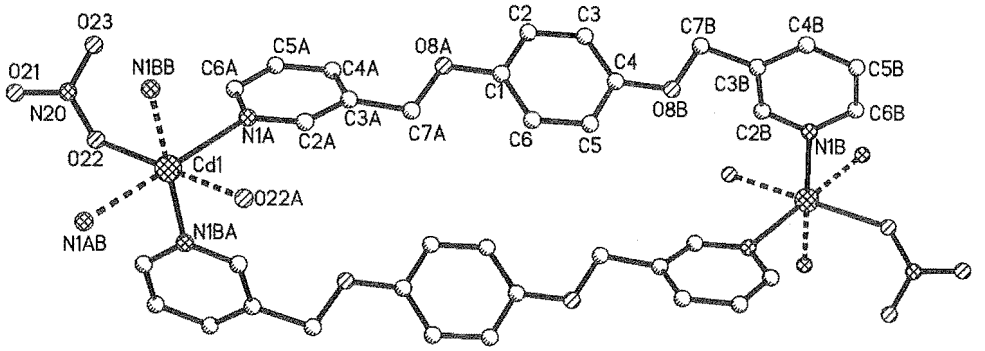


Figure 3.23 Perspective view of **3.32**, with atomic labelling shown; hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and bond angles (°): Cd1-N1BA 2.303(2), Cd1-O22 2.367(2), Cd1-N1A 2.369(2), N1B-Cd1-O22 96.30(8), N1B-Cd1-N1A 91.88(9), O22-Cd1-N1A 95.68(8).

inversion, and is coordinated by four pyridine nitrogen atoms and two nitrate oxygens. The Cd-N and Cd-O bond distances are similar [Cd1-N1B 2.303(2)Å, Cd1-N1A 2.369(2)Å and Cd1-O22 2.367(2)Å], and, as a consequence of the centre of inversion, the coordination geometry of the cadmium is octahedral. The coordinated oxygen atoms are 0.14Å closer in

this structure than in the structure of **3.29** above, as the d^{10} Cd(II) atom is not subject to Jahn-Teller distortions.

The similarity of this structure to that of the copper(II) nitrate structure **3.32** also extends to the conformation of the ligand. The pyridine rings are tilted at an angle of 80.1(1)° to each other and at angles of 30(1)° and 74(1)° to the central benzene ring. These values are within 5° of the corresponding values for the copper(II) complex described above, showing the ligands are in a similar conformation. As with the copper structure above the pyridine rings of the macrocycle are in a *cis*-relationship on the metal atom, and this, combined with the conformation of the ligand means that there can be no interactions between the ligands of the macrocycle. The distance between the cadmium atoms across the macrocycle is 16.647(1)Å, which is 4% larger than the distance between the metal centres across the macrocycle in the analogous copper complex.

The 'necklace' polymers of **3.32** pack in an almost identical fashion to the copper(II) nitrate complex **3.29**. The polymers propagate along the *ac*-diagonal, and stack down the *a*-axis of the unit cell. The distance between cadmium atoms in the stacks is 8.351(1)Å. The M_2L_2 macrocycles of the 'necklace' polymer are not interpenetrated, and there are no solvate molecules contained within the cavity. This is due to the *cis*-relationship of the pyridine rings of the macrocycle and the conformation of the ligand.

The 'necklace' topology observed in the cadmium and copper(II) nitrate structures of **3.25** is not uncommon in coordination chemistry. The topology, which is represented in figure 3.24, requires two bidentate ligands that can form a macrocyclic structure, and a metal atom that can join at least four ligands. The use of rigid ligands with the donor atoms oriented at an angle, such as 1,1-bis(4-pyridyl)ethane, which allows macrocycle formation has been combined with multicoordinate metals, such as cadmium nitrate, to give the

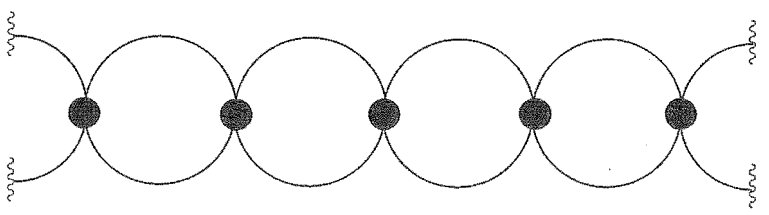


Figure 3.24 Cartoon representation of the topology of the 'necklace' polymer structure of **3.29** and **3.32**.[†]

[†] Throughout this thesis the cartoon representations will use filled black circles to indicate metal atoms, and black lines to represent ligand molecules.

necklace topology.[78] Flexible ligands, which have the conformational freedom to adopt macrocyclic structures, such as 1,6-bis(4-pyridyl)hexane, have given a 'necklace' topology when combined with copper(II) nitrate.[111] When the flexible ligand bis(4-pyridyl)disulfide was combined with CuI, an interesting 'necklace' polymer was formed, which involves a tetrahedral metal cluster.[112]

Interpenetration and encapsulation of solvent in polymers requires structures with large cavities.[18] These cavities can be occupied by other polymeric strands, for interpenetration, or by solvate molecules or noncoordinated ions, for encapsulation. The flexibility of **3.25**, and the other ligands used in this study, make them less likely to form such structures, as these ligands have the conformational freedom to allow the formation of structures without cavities. It seems that it is possible for the flexibility to allow the ligand to adopt conformations which restrict the amount of space free for encapsulation or interpenetration.

Crystal structure of **3.33**

The zinc bromide complex, **3.33**, has a one-dimensional polymeric structure. The complex crystallizes in the monoclinic space group $P2_1/n$ with one molecule of **3.25** and one zinc bromide in the asymmetric unit, as shown in figure 3.25. The ligand, **3.25**, again

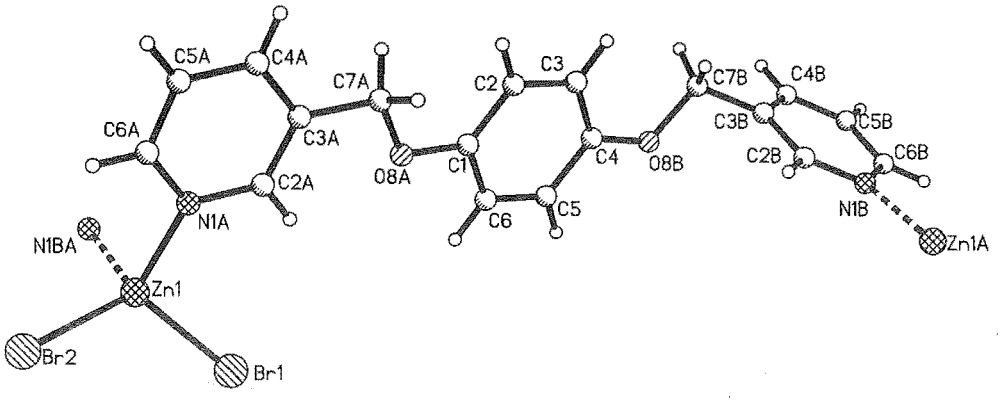
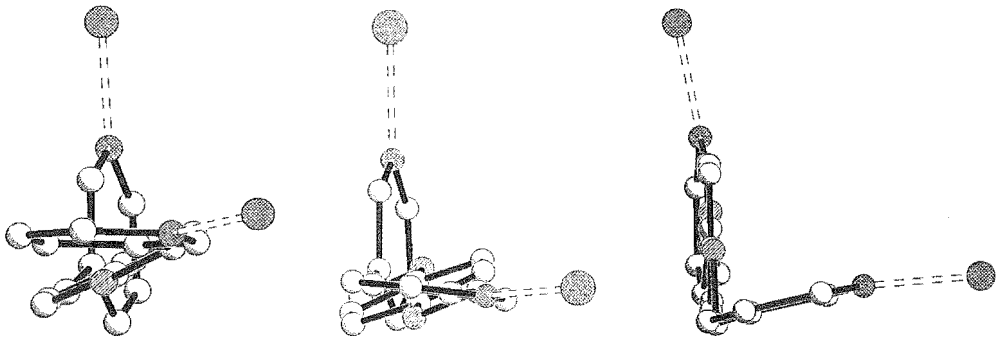


Figure 3.25 Perspective view of the structure of **3.33**, with atomic labelling shown. Selected bond lengths (Å) and bond angles (°): Zn1-N1A 2.048(3), Zn1-N1BA 2.056(3), Zn1-Br1 2.3518(8), Zn1-Br2 2.3639(8), N1A-Zn1-N1BA 96.7(1), N1A-Zn1-Br1 107.41(7), N1BA-Zn1-Br1 112.84(8), N1A-Zn1-Br2 115.44(8), N1BA-Zn1-Br2 104.60(7), Br1-Zn1-Br2 117.93(3).

bridges two metal atoms, however, unlike the structures **3.29** and **3.32** above, the polymer does not contain spiro-macrocyclic units. This is due to the zinc bromide being four-coordinate, with two sites occupied by bromine atoms and two by nitrogen atoms of different bridging ligand molecules. The Zn-N bond lengths are 2.048(3)Å and 2.056(3)Å. The coordination geometry of the zinc is approximately tetrahedral (largest deviation the N-Zn-N angle of 96.7(1)°).



(a) (b) (c)

Figure 3.26 View of the twist of the bridging ligand **3.25** in the structures of **(a) 3.29, (b) 3.32, (c) 3.33**

The conformation of the ligand in **3.33** is similar to that of the $Cu(NO_3)_2$ and $Cd(NO_3)_2$ complexes above, with the meanplanes of the pyridine groups inclined at angles of 4.8(1)° and 101.8(1)° to the benzene ring. In the two 'necklace' polymer structures above the ligand bridges the metal atoms with twists of 90.4(1)° and 91.9(1)°, respectively. This twist is shown in figures 3.26(a) and 3.26(b), respectively. The twist allows the *cis* oriented ligands to form M_2L_2 macrocycles. In the structure of **3.33** the ligand is also twisted at an angle of 96.7(1)°, as shown in figure 3.26(c). However, this twist is not enforced by the coordination geometry of the metal atom. This similarity is remarkable considering the large number of possible conformations available to the flexible ligand **3.25**, which has six single bonds about which there is the possibility of free rotation. In the other structures studied with this ligand, **3.27** and **3.31**, the ligand does not adopt such a twist as it resides with the centroid of the benzene on a centre of inversion.

The polymeric chains of **3.33** propagate along the *ac*-diagonal, similar to the 'necklace' polymers above. The polymeric strands are involved in numerous π-π face-to-face and two π-π edge-to-face interactions, as shown in figure 3.27. The benzene ring of

the ligand (**3.25**) is involved in face-to-face interactions with pyridine rings of adjacent strands. The coplanar pyridine-benzene arm of the ligand is related to another through a centre of inversion, giving an almost coplanar [4.8(1)°] face-to-face interaction, with the centre of the N1A-C6A bond 3.376(4)Å away from the plane of the benzene ring. The other pyridine arm of the ligand is also involved in a face-to-face interaction to a benzene ring. This ring is less coplanar [16.6(1)°], and the closest approach is further away [3.572(2)Å], indicating a weaker π-π interaction. The edge of the benzene ring is suspended above, and almost perpendicular to [85.8(1)°], a pyridine ring, with the closest interaction between H3 and the meanplane, 2.99(4)Å apart.

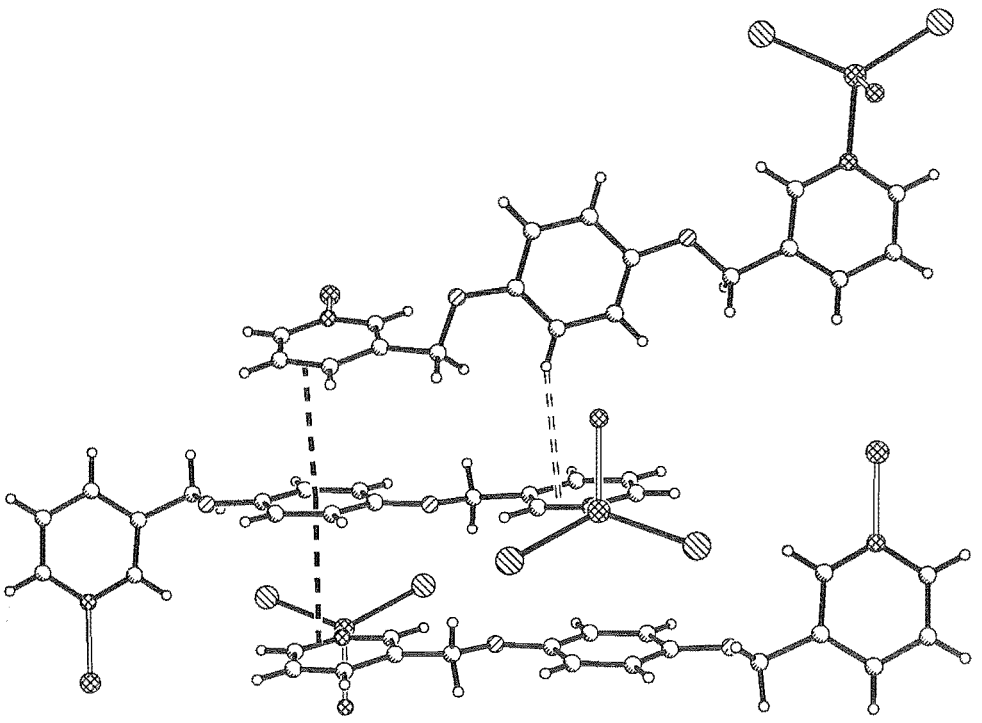


Figure 3.27 Perspective view of the π-π face-to-face and edge-to-face interactions of the polymeric chains in **3.33**. The face-to-face interactions are show as solid dashed lines, and the edge-to-face interaction is shown as a hollow dashed line.

3.4.3 Coordination complexes of 3.26

The coordination chemistry of **3.26** was investigated with the formation of complexes with $AgBF_4$ (**3.34**), $PdCl_2$ (**3.35**), $Cu(NO_3)_2$ (**3.36**), CuI (**3.37**), $Cd(NO_3)_2$ (**3.38**) and $ZnBr_2$

(3.39). The reaction of 3.26 with $AgBF_4$ in acetonitrile gave a white solid, 3.34, which analysed as [$AgBF_4$.(3.26).1½CH_3CN]. Although this complex was soluble in various solvents, an NMR spectrum of this complex showed only noncoordinated ligand. Despite numerous attempts no crystals of this complex could be grown. No further analysis was attempted.

The palladium chloride complex, 3.35, and the zinc bromide complex, 3.39, were isolated from the reactions of **3.26** with Li_2PdCl_4 and $ZnBr_2$ in methanol, respectively. These complexes analysed as [M.(**3.26**)], with M = $PdCl_2$ for 3.35 and M = $ZnBr_2$ for 3.39. The complexes were both insoluble in common solvents and, given the likelihood of **3.26** acting as a bridging ligand, this and the analysis might indicate polymeric structures. No further investigation was undertaken.

The reaction of **3.26** with copper(II) nitrate in methanol gave a blue crystalline solid, **3.36,** which analysed with a 1:1 metal-ligand stoichiometry. This stoichiometry is different to the copper(II) nitrate complex of **3.25** above, which had a 'necklace' polymer structure. This stoichiometry could indicate an oligomeric or polymeric structure for **3.36**, and crystals suitable for single crystal X-ray analysis were grown by careful layering of a solution of $Cu(NO_3)_2$ in methanol onto a dichloromethane solution of **3.26**.

The copper(I) iodide complex, **3.37**, was isolated from the reaction of **3.26** with CuI in acetonitrile as a white crystalline solid. This solid analysed as [Cu_2I_2.(**3.26**).½CH_3CN], and was insoluble in common solvents. The stoichiometry, coupled with the general insolubility, could indicate that **3.37** has a polymeric structure.

The reaction of **3.26** with cadmium nitrate gave a colourless crystalline solid **3.38**, which analysed as [$(Cd(NO_3)_2)_3$.$(\mathbf{3.26})_4$.MeOH]. Crystals suitable for X-ray structure analysis were grown via slow evaporation of a methanol solution of **3.38**, to determine the structure of this complex.

Crystal structure of 3.36

Complex **3.36** crystallizes in the centrosymmetric triclinic space group P-1, and has a one-dimensional polymeric structure. The asymmetric unit contains one molecule of **3.26**, one copper(II) nitrate, and disordered dichloromethane and methanol solvate molecules. The ligand bridges two copper atoms, as shown in figure 3.28. The pyridine rings of **3.26** are slightly inclined to the benzene ring, with angles of 11.7(1)° and 10.0(1)°, giving the ligand a relatively planar overall conformation (mean deviation 0.108(4)Å for all the non-

hydrogen atoms). In this extended conformation the ligand forms a linear bridge between two copper atoms separated by 19.463(1)Å.

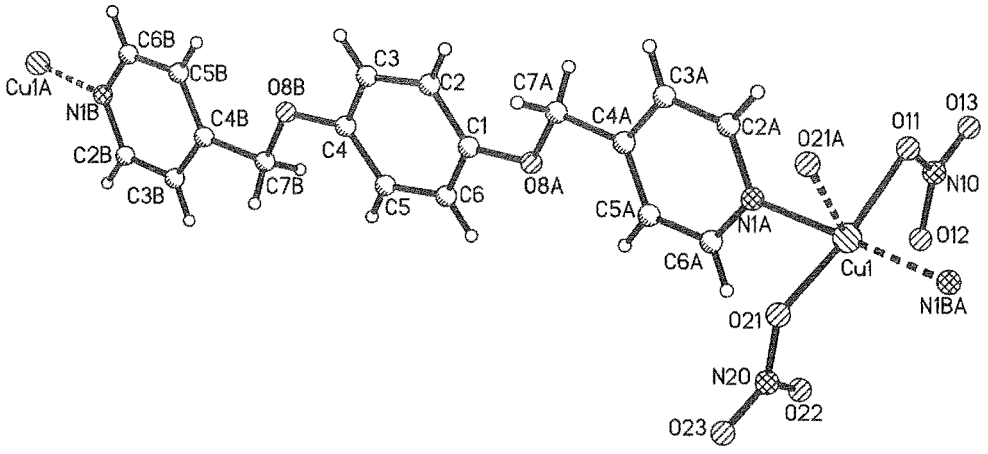


Figure 3.28 Perspective view of **3.36**, with the longer Cu-O bond shown as dashed. Disordered solvate molecules has been removed for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-O11 1.994(2), Cu1-O21 2.004(2), Cu1-N1BA 2.006(2), Cu1-N1A 2.006(2), Cu1-O21A 2.446(2), O11-Cu1-O21 168.28(7), O21-Cu1-N1B 91.25(9), O21-Cu1-N1A 89.98(9), N1B-Cu1-N1A 176.26(9), O21A-Cu1-O21 74.28(8), O21A-Cu1-O11 94.02(7).

The copper atoms of **3.36** have a square pyramidal geometry and are coordinated by two nitrogen atoms of **3.26**, and three nitrate oxygen atoms. The nitrogen atoms of **3.26** are *trans* in the basal plane, with Cu-N bond lengths of 2.006(2)Å and 2.006(2)Å, which are identical only by coincidence. Two of the oxygen atoms are bifurcated between two copper atoms forming a Cu_2O_2 ring, as shown in figure 3.29. Two Cu_2O_2 rings are bridged by two molecules of **3.26**, giving a 38-membered $Cu_4O_2L_2$ macrocycle. The Cu_2O_2 rings are formed by one basal plane oxygen and an apical oxygen atom, with Cu-O bond lengths of 2.004(2)Å and 2.446(2)Å, respectively. The Cu···Cu distance is 3.558(2)Å and the Cu1-O21-Cu1A angle is 105.72(8)°, with the centre of the Cu_2O_2 ring lying on a centre of inversion. The remaining basal site is occupied by the oxygen atom of a monodentate nitrate anion with a C-O bond length of 1.994(2)Å.

The Cu_2O_2 structural motif is reasonably common for dimeric structures,[61] with most examples involving bridging oxide or hydroxide anions, or water molecules. Bifurcated nitrate bridges are much less common, with only five other examples known. Of these

examples, three are dimeric, two with monodentate ligands,[113] and one in which the ligand bridges the two copper atoms.[101] The remaining two examples are polymeric, one with 2,2-bipyrimidine as a bridging chelating ligand.[114] The other has a structure similar to **3.36**, involving two 1,2-bis(4-pyridyl)ethyne molecules bridging Cu_2O_2 rings to form a ladder polymer.[115] These examples have similar geometries to **3.36**, with Cu···Cu distances in the range 3.418 – 3.766Å.

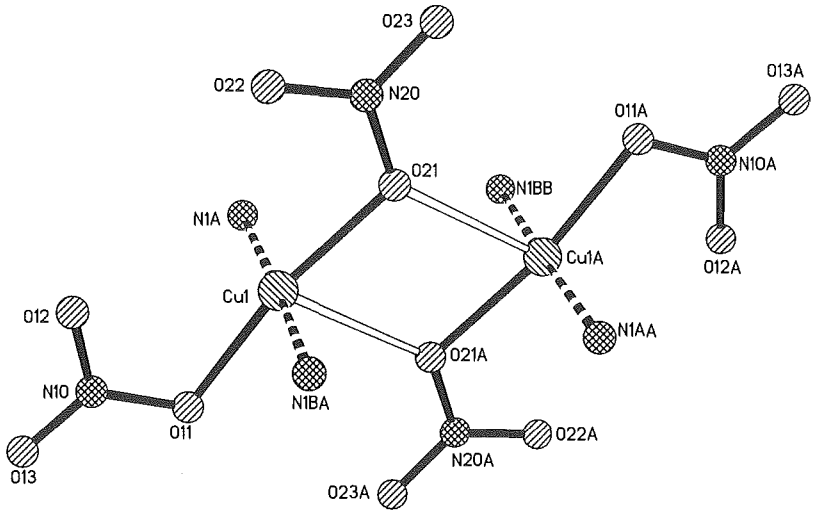


Figure 3.29 Perspective view of the Cu_2O_2 ring and copper coordination sphere of **3.36**. The longer apical Cu-O bonds are shown as hollow.

The ligand molecules of the 38-membered $Cu_4O_2L_2$ macrocycle are related by an inversion centre which lies at the centre of the 38-membered ring. The ligands of the macrocycle arrange with the pyridine rings offset stacked and slightly tilted at an angle of 3.9(1)° to one another. The centre of the C2-C3 bond of one pyridine is 3.55(2)Å above the centroid of the pyridine of the opposite ligand, as shown in figure 3.30. The benzene rings of the macrocycle are coplanar, due to the centre of inversion, with the meanplanes of the rings 3.80(2)Å apart, indicating a weaker π-π face-to-face interaction than occurs between the pyridine rings.

The 'ladder' polymeric strands of **3.36** stack in columns, with the spaces between the strands occupied by dichloromethane and methanol solvate molecules. The asymmetric unit of **3.36** contains two sites occupied with solvate, one is occupied with dichloromethane, while at the other the occupancy is shared between dichloromethane and methanol in a 7:1 ratio. The space occupied by the solvate molecules is sufficiently large to preclude any interactions between the polymer chains.

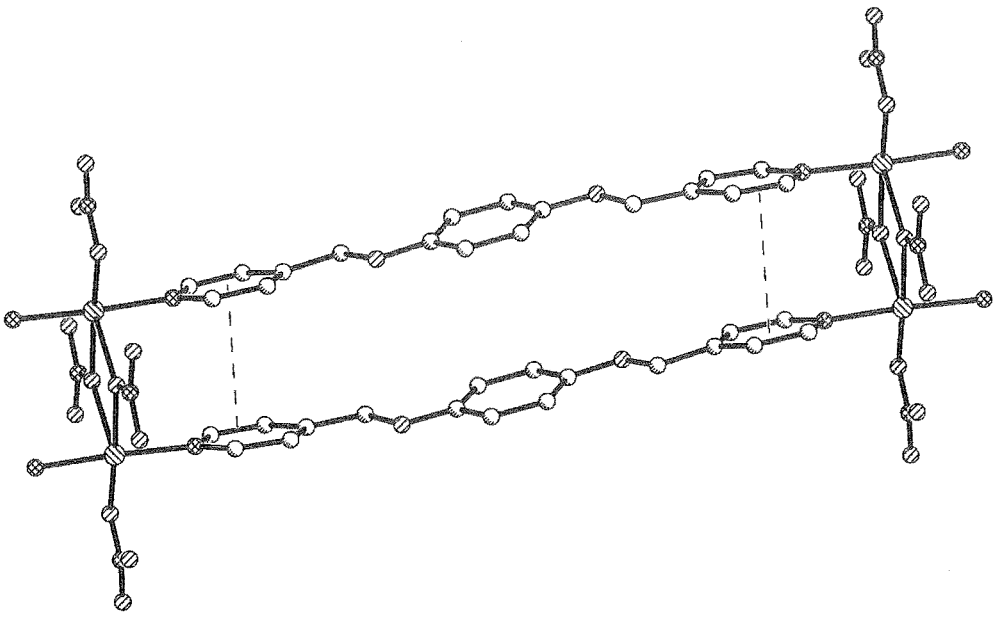


Figure 3.30 View of the $Cu_4O_2L_2$ macrocycle of **3.36**, with the stacking between C2-C3 and the centroid of the pyridine rings shown. The hydrogen atoms have been omitted for clarity.

Crystal structure of **3.38**

The cadmium nitrate structure, **3.38**, crystallizes in the centrosymmetric triclinic space group P-1. The complex analysed with an intriguing 4:3 ligand-metal stoichiometry, and in accord with this the asymmetric unit of **3.38** was found to contain two molecules of **3.26**, one and one half cadmium nitrates and some disordered methanol and water solvate molecules. The structure of **3.38** contains two separate one-dimensional polymers with different topologies within the same complex. The polymers have ligand-metal stoichiometries of 1:½ and 1:1, which combine to give the overall stoichiometry of 4:3.

The polymer with 1:½ stoichiometry is one-dimensional and is made up of spiro-macrocycles. This 'necklace' polymer has a similar topology to the structures of **3.29** and **3.32** described above. One of the macrocyclic units is shown in figure 3.31. The octahedral cadmium atoms lie on centres of inversion, and are coordinated by the pyridine groups of four ligands and the oxygen atoms of two nitrate anions. The Cd-N bonds are 2.347(5)Å and 2.400(6)Å long, and the Cd-O bond length is 2.417(6)Å.

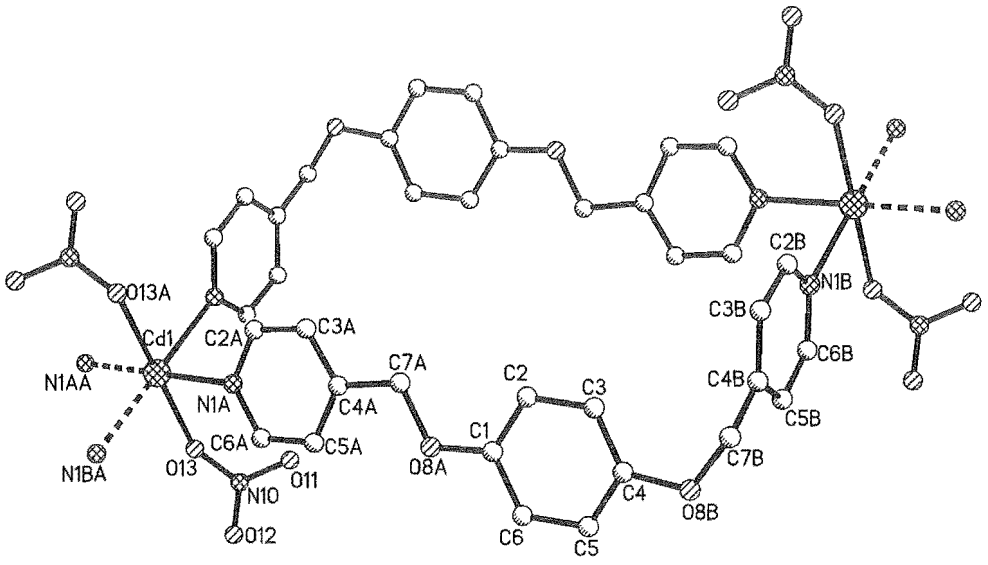


Figure 3.31 Perspective view of the 'necklace' polymer component of the structure of **3.38**, with atomic labelling shown; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cd1-N1A 2.347(5), Cd1-N1BA 2.400(6), Cd1-O13 2.417(6), N1A-Cd1-N1BA 88.1(2), N1BA-Cd1-N1AA 92.0(2), N1A-Cd1-O13 97.4(2), N1AA-Cd1-O13 82.6(2), N1BA-Cd1-O13 87.8(2), N1AA-Cd1-O13 92.2(2).

The necklace polymer component of **3.38** is constructed from 34-membered macrocycles, with the bridged cadmium atoms 15.561(3)Å apart. The two bridging molecules of **3.26** in the macrocycle are L-shaped, with one of the pyridine rings inclined at an 84.3(9)° angle to the benzene ring. This results from the fact that one arm of the ligand exists in the extended *anti* conformation, while the other arm has a *gauche* conformation of the side chain. The L-shaped ligands of the macrocycle combine to form a rectangular box. The box is defined by the distance between the centroids of the pyridine rings [13.59Å] and the distance between the bridging methylene groups of the long arm of the ligand [7.19Å], giving a box with 97.75Å^2 area. The macrocycle forms around the disordered water and methanol solvate molecules.

The 1:1 polymer component of the structure of **3.38** has a 'ladder' topology, similar to that of **3.36**. The ligand molecule, **3.26**, bridges two cadmium atoms at a distance of 20.274(3)Å, as shown in figure 3.32. The ligand is largely planar, with the pyridine rings slightly inclined at angles of 6.9(9)° and 7.3(9)° to the benzene ring, with both arms of the ligand having the extended *anti* conformation. However, the methylene groups of the

$-CH_2O-$ spacer of **3.26** are in a '*cisoid*' conformation relative to the benzene ring, which is a different conformation compared to the '*transoid*' conformation of the spacer groups of the ligand in the structure of **3.36**.

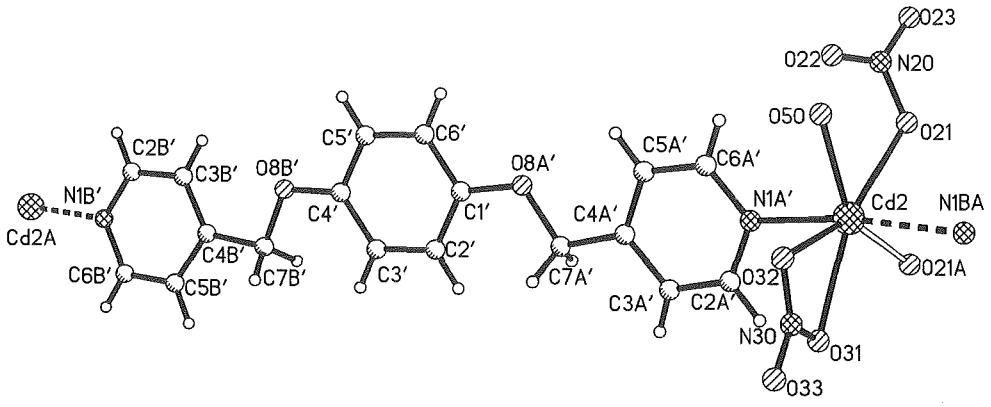


Figure 3.32 Perspective view of the ligand in the 'ladder' polymer component of **3.38**, with atomic labelling shown. The hydrogen atoms of the water molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd2-N1A' 2.299(6), Cd2-N1BA 2.303(6), Cd2-O31 2.432(7), Cd2-O21 2.476(6), Cd2-O21A 2.512(7), Cd2-O32 2.5521(3), Cd2-O50 2.55(1), N1A'-Cd2-N1BA 168.1(2), N1A'-Cd2-O31 89.5(2), N1A'-Cd2-O21 93.8(2), O31-Cd2-O21 160.3(2), O31-Cd2-O32 50.8(3), O21-Cd2-O32 147.4(4), O31-Cd2-O50 114.4(3), O21-Cd2-O50 83.7(3), O32-Cd2-O50 63.8(4), N1A'-Cd2-O50 103.6(3), N1BA-Cd2-O50 88.2(3).

The cadmium atoms of the 'ladder' polymer are hepta-coordinate, with a pentagonal bipyramidal geometry. The pyridine groups of **3.26** are *trans* and occupy the apical sites, with Cd-N bond lengths of 2.299(6)Å and 2.303(6)Å. The pentagonal plane is occupied by a chelating nitrate anion, two bifurcated oxygen atoms of nitrate anions and the oxygen of a water molecule. The Cd-O bond lengths lie in the range 2.432(7) – 2.552(3)Å, with the longest bond to the water molecule. Two cadmium atoms are bridged by two bifurcated oxygen atoms of nitrate anions to form a Cd_2O_2 macrocycle similar to the Cu_2O_2 macrocycle in the structure of **3.36**, as shown in figure 3.33. The centroid of the Cd_2O_2 macrocycle lies on a centre of inversion, and the Cd-O bond lengths are similar [2.476(6) and 2.512(7)Å], with a O-Cd-O angle of 85.6(9)°, giving the macrocycle a slightly distorted square shape. The Cd···Cd distance across the square is 4.121(3)Å.

Cd_2O_2 rings are less common than Cu_2O_2 rings, which could simply reflect the lower number of structure determinations of cadmium containing compounds. Similar to the pattern of Cu_2O_2 rings, water is the most common bifurcating molecule to form this type of ring system. Two examples exist of Cd_2O_2 rings with nitrate anions providing both the bifurcating oxygens. These consist of a dimeric structure involving a large amine containing macrocycle,[116] and a one-dimensional polymeric structure.[117] The polymeric structure is formed from *trans*-1,2-bis(4-pyridyl)ethene, which is a more rigid molecule, similar to the ligand **3.26**. Both these structures have similar Cd_2O_2 geometries with Cd···Cd distances of 4.17Å and 4.29Å, respectively. The Cd_2O_2 squares are bridged by two ligands to give a 38-membered $Cd_4O_2L_2$ macrocycle similar to the structure of **3.36**, as shown in figure 3.33. The pairs of **3.26** which make up the 38-membered macrocycle arrange stacked on top of one another, with the pyridine rings almost coplanar, at an angle of 10.9(9)° to one another. The centroid of one of the pyridine rings lies 3.71(1)Å above the N1'-C6' bond. The ligands of the 'ladder' are related by a centre of inversion which lies at the centre of the macrocycle. The coplanar benzene rings arrange with the centroid of one lying 3.58(1)Å above the C1'-C2' bond, indicating a stronger π-π interaction than occurs between the pyridine rings.

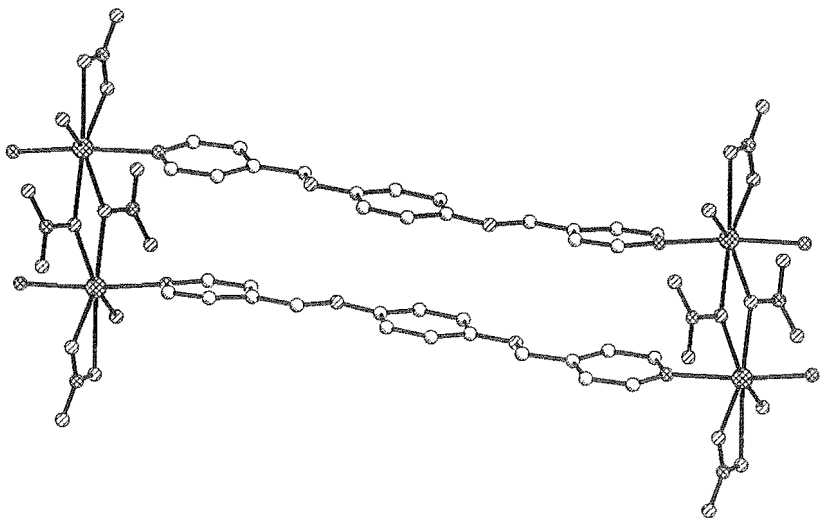


Figure 3.33 View of the 38-membered $Cd_4O_2L_2$ macrocycle of the 'ladder' polymer component of **3.38**. The hydrogen atoms have been omitted for clarity.

The polymeric chains of **3.38** stack in layers perpendicular to the *b*-axis of the unit cell. The layers contain only polymers of one stoichiometry, giving alternating layers of 'necklace' and 'ladder' polymers. The different chains propagate in slightly different

directions, with the 'necklace' polymer propagating along the *a*-axis, while the 'ladder' propagates along the *ac*-diagonal. The angle between the topologically different chains is 31°.

The polymers interact with adjacent chains, both within a layer and with the adjacent two layers. The planar 'ladder' polymers are tilted so that there can be no π-π interactions between polymers of the same layer. The 'ladder' polymers are offset, so that the nitrate anions of one strand are adjacent to the methylene groups of another strand. However, the oxygen atoms of the nitrate anions are too far away for any interactions to occur. The 'necklace' polymer strands form a tiled arrangement, so that the long edge of the rectangular macrocycles are adjacent. This arrangement does not allow any π-π interactions as the strands form with the aromatic rings adjacent to the $-CH_2O-$ spacer groups. The aromatic rings of adjacent layers are almost perpendicular, allowing only π-π edge-to-face interactions to occur. However, the strands of adjacent layers do not form with sufficient proximity to allow any interactions of this type. There are many weak interactions between the nitrate counterions of the layers and water solvate molecules, the H···O distances all lie within the range 2.49(9) – 3.00(9)Å. The coordinated water molecules of the 'ladder' polymer form above and below the solvate-containing cavity of the 'necklace' macrocycle and are oriented into the cavity of the macrocyle. The interactions between the water and methanol solvate molecules and the adjacent coordinated water are only poorly determined due to disorder of the solvate molecules.

The presence of two different structures with the same starting components in the same crystal is a rare occurrence. The ability for both structures to occur in the same crystal represents small differences in energy between the two structures, so that the loss of symmetry involved in forming a crystal with two chemically different structures can be overcome by the interactions between the structures. The occurrence of different structures of discrete inorganic complexes has been observed, with the occurrence of two isomers within the same crystal in a Rh complex[118] and in two Ni complexes.[119] The coexistence of coordination polymers with other species has also been observed. The reaction of pyridazine with silver nitrate gives a structure containing a helical coordination polymer and stacked M_2L_2 macrocycles.[120] The reaction of the flexible ligand 1,3-bis(1-pyrazolyl)propane with silver nitrate gives a structure containing both a polymer and discrete metallocycles.[85] The interpenetration of different polymers and nets has been observed to encapsulate solvate molecules.[121]

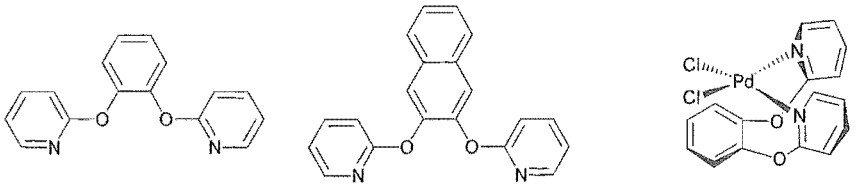
The formation of the first structure containing two different isomeric one-dimensional polymers which are not interpenetrating was achieved using the flexible ligand 2,5-bis(2-pyridylmethylsulfanylmethyl)pyrazine, which, when mixed with silver nitrate, gives a structure with two topologically different polymers.[99] The authors of this paper use the term 'topological isomorphism'[112] to describe the different polymeric chains, which have the same constituents, but which differ in connectivity of the silver atoms. The formation of two different polymers, one involving only metal-ligand coordination, the other involving hydrogen bonding, was observed for a silver isonicotinate complex.[122] The structure of the cadmium nitrate complex **3.38** appears to be the first example of two non-interpenetrated polymers which have different topologies and stoichiometries.*

The complexes formed from the molecules **3.25** and **3.26** show the versatility of these ligands. The two ligands, which both involve a 1,4-disubstituted benzene ring, were found to effectively bridge two metal atoms. The flexibility of the ligand design allowed the formation of macrocyclic fragments, although these could not be isolated as discrete species. It was decided at this point to investigate flexible ligands, similar to those above, which are predisposed to the formation of macrocyclic species as a consequence of the substitution pattern of the aromatic core.

3.5 Catechol based $-CH_2O-$ ligands

The formation of complexes containing a catechol group has been an area of intense interest. The ability of catechol to chelate metal atoms is utilised by some 'siderophoric' molecules, such as enterobactin, which is used as an iron storage molecule by bacteria.[123] Ligands constructed with catechol groups attached to coordinate metal atoms form numerous complexes, including cages and helicates.[124] Flexible ligands with cores constructed from catechol, such as those shown in figure 3.34(a), have been prepared by members of the Steel group to investigate their metallosupramolecular chemistry.[102,107] These molecules were found to chelate metal atoms in the majority of cases, with the palladium complexes having the structure shown in figure 3.34(b).

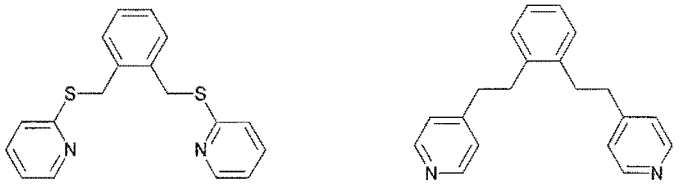
* After submission of the author was made aware of the publication of this structure, see H. Hou, Y. Fan, L. Zhang, C. Du, and Y. Zhu, *Inorg. Chem. Commun.*, **2001**, *4*, 168. Thanks to Dr Lyall Hanton for this information.



(a) (b)

Figure 3.34

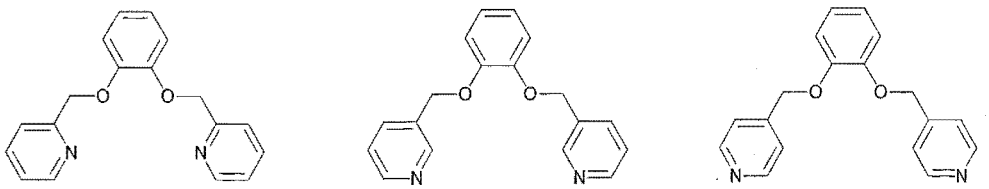
Ligands with 1,2-disubstituted cores have been investigated by the formation of the potential ligands shown in figure 3.35. Despite the possibility of these molecules forming discrete complexes, thus far only coordination polymers have been structurally characterised. The silver nitrate complex of 1,2-bis(2-pyridylsulfanylmethyl)benzene (fig 3.35(a)) has a 1-D polymeric structure, with the sulfur atom of the chain interacting with the silver atoms.[125] The cadmium nitrate complex of 1,2-bis(4-pyridylethyl)benzene (fig 3.35(b)) has a 2-D sheet-like structure.[79]



(a) (b)

Figure 3.35

As an extension of these studies the potential ligands **3.40 – 3.42**, shown in figure 3.36, were synthesised to investigate their coordination chemistry.



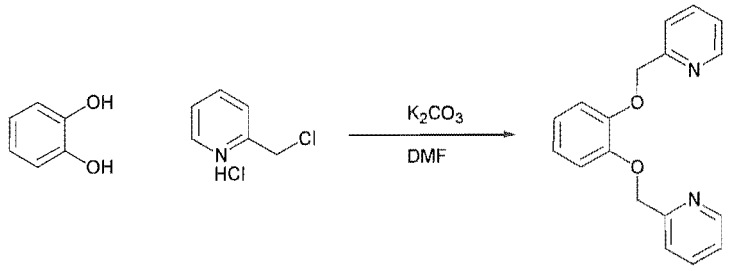
3.40 **3.41** **3.42**

Figure 3.36

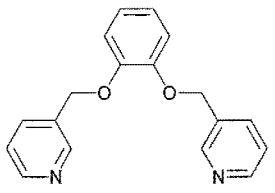
3.5.1 Ligand Synthesis

The ligands 1,2-bis(2-pyridylmethoxy)benzene (**3.40**), 1,2-bis(3-pyridylmethoxy)-benzene (**3.41**) and 1,2-bis(4-pyridylmethoxy)benzene (**3.42**) were synthesised in a method

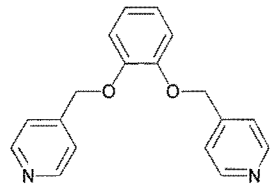
analogous to that of O'Keefe, as shown in scheme 3.4. Catechol, two equivalents of 2-, 3- or 4-chloromethylpyridine hydrochloride and potassium carbonate were warmed in N,N-dimethylformamide. The resulting products were purified by chromatography to give **3.40**, **3.41** and **3.42** in 48%, 24% and 22% yields, respectively. The lower yields of **3.41** and **3.42** might be due to formation of oligomeric and polymeric N-alkylpyridine species.[126] This would be less likely to occur with 2-chloromethylpyridine, as the proximity of the alkyl group would increase the steric hindrance of the pyridine nitrogen atom.



3.40



3.41



3.42

Scheme 3.4

3.5.2 Coordination complexes of 3.40

The coordination chemistry of **3.40** was investigated by the formation of complexes with $AgNO_3$ (**3.43**), $CuCl_2$ (**3.44**), $Cd(NO_3)_2$ (**3.45**) and $ZnBr_2$ (**3.46**). The silver nitrate complex, **3.43**, was isolated by diffusion of ether into a methanol solution containing **3.40** and silver nitrate. The crystals obtained by ether diffusion into the reaction mixture were suitable for X-ray structure analysis. An elemental analysis of these crystals showed they had a formula corresponding to [$AgNO_3$.(**3.40**)].

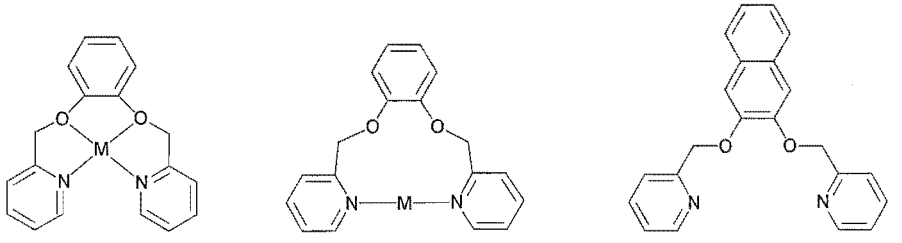
The reaction of **3.7** with copper(II) chloride in methanol gave **3.44** as a green solid. This solid was soluble in DMF and H_2O, and analysed as [$CuCl_2$.(**3.40**)]. Large green crystals suitable for X-ray single crystal structure determination were obtained by careful layering of a methanol solution of $CuCl_2$ onto a dichloromethane solution of **3.40**.

The reaction of **3.40** with cadmium nitrate in methanol gave a white precipitate (**3.45**), which analysed with a 1:1 metal-ligand stoichiometry. An NMR analysis of this solid,

which was soluble in DMSO, showed only noncoordinated ligand. No further analysis was undertaken.

The zinc bromide complex, **3.46**, was prepared by reaction of **3.4** with $ZnBr_2$ in methanol. The precipitate that formed analysed with a 1:1 metal-ligand stoichiometry. The complex was soluble in donating solvents such as DMSO, and an NMR analysis showed only noncoordinated ligand in solution. The analysis for this complex is consistent both with the zinc atoms being chelated by **3.40** and various polymeric species. No further analysis was undertaken.

The arrangement of the nitrogen donor atoms in **3.40** allows the possibility that this ligand can chelate a metal atom between the two pyridine atoms, with or without the involvement of the oxygen donors, as shown in figure 3.37(a) and 3.37(b), respectively. The coordination complexes of the related ligand 2,3-bis(2-pyridylmethoxy)naphthalene (fig 3.37(c)) were investigated by O'Keefe.[102] The silver nitrate complex was tetradentate, while the copper(II) chloride complex was bidentate.



(a) (b) (c)

Figure 3.37 Possible coordination modes of **3.40**, **(a)** tetradentate, **(b)** bidentate. **(c)** 2,3-Bis(2-pyridylmethoxy)naphthalene

Crystal structure of **3.43**

The silver nitrate complex, **3.43**, crystallizes in the triclinic space group P-1. The asymmetric unit contains four ligand molecules (**3.40**) and four silver nitrates. The structure involves each ligand chelating a silver atom through the nitrogens of the pyridine rings; one of the ligand-metal units is shown in figure 3.38. The four mononuclear units of **3.43** differ considerably in the conformations of the chelating ligand, and the interactions between the silver atoms and the oxygens of the nitrate counterions. The ligands each chelate a silver atom to form an 11-membered metallocycle. The Ag-N bond lengths range between 2.192(2)Å and 2.265(2)Å, with the silver atoms having a distorted linear

geometry with N-Ag-N bond angles in the range 156.7(2) – 163.3(2)°. These distortions indicate that the silver atoms are attracted to the ether oxygen atoms of the ligand molecules, with Ag···O distances between 2.611(2)Å and 2.679(2)Å.

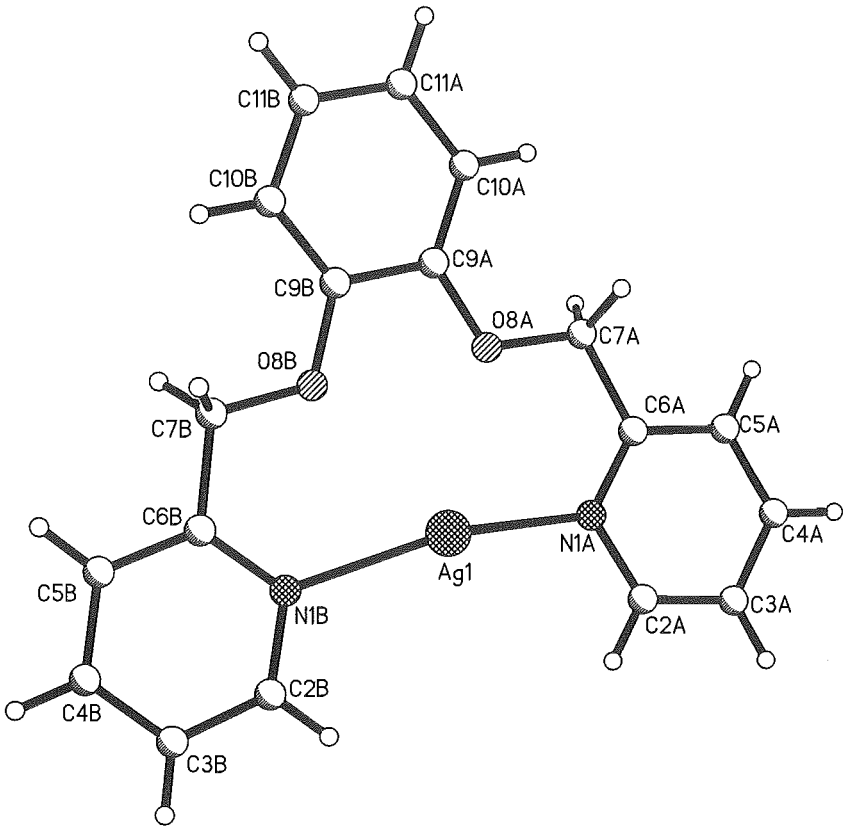


Figure 3.38 Perspective view of one of the mononuclear units of **3.43.**

The nitrate counterions occupy spaces between the mononuclear units. Each of the counterions interacts with a silver atom through an oxygen. Three of these interactions are in the range 2.883(2) – 2.993(2)Å. The fourth interaction is considerably closer with an Ag···O distance of 2.678(2)Å, which, in part, destroys any higher symmetry relationships between the mononuclear units. The oxygen atoms of the nitrate counterions are also involved in C-H···O interactions with the ligand, with H···O distances between 2.405(4)Å and 2.939(4)Å.

The packing of the mononuclear units is characterised by numerous π-π face-to-face interactions between planar aryl and pyridine rings of the ligands. These interactions typically involve rings which are almost coplanar (meanplanes tilted by <15°) with the

overlapping typically offset by half an aryl or pyridine ring. This is, as stated above, the most energetically stable arrangement. The closest interactions lie between 3.4Å and 3.8Å.

Crystal structure of **3.44**

The copper(II) chloride complex crystallizes in the monoclinic space group C2/c, with half a ligand molecule (**3.40**) and half a copper(II) chloride in the asymmetric unit. The complex has a mononuclear structure, which is shown in figure 3.39. The two halves of the molecule are related by a two-fold rotation axis which passes through the copper atom and

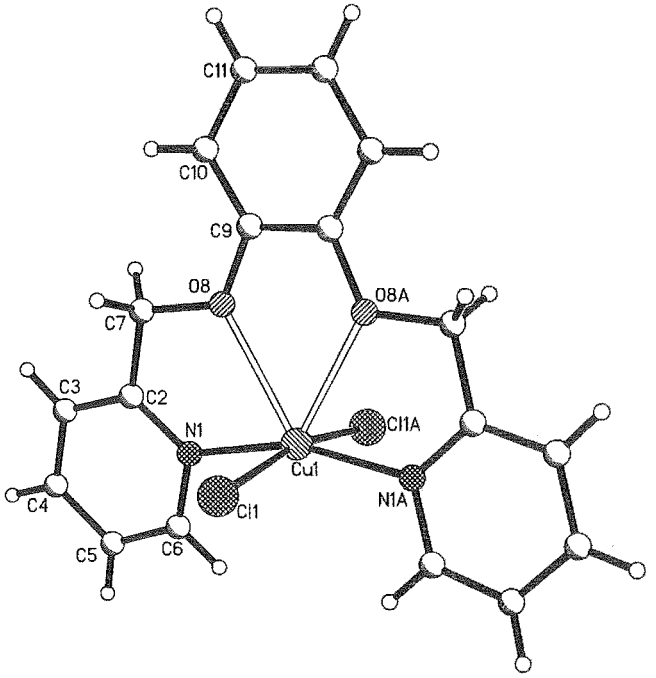


Figure 3.39 Perspective view of the mononuclear structure of **3.44**. The longer bonds to the oxygen atoms are shown as hollow. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.045(4), Cu1-Cl1 2.299(1), Cu1-O8 2.503(3), N1A-Cu1-N1 160.6(2), Cl1-Cu1-Cl1A 167.34(7), O8-Cu1-O8A 60.0(1), N1-Cu1-Cl1 88.0(1), N1-Cu1-Cl1A 89.9(1), O8-Cu1-Cl1 94.0(1), O8-Cu1-N1 69.7(1).

centroid of the benzene ring. The ligand wraps around the metal and is tetradentate, coordinating the copper atom through the pyridine nitrogen atoms and ether oxygen atoms. The copper atom is also coordinated by two chlorine atoms. The Cu-N bond length of 2.045(4)Å, and the Cu-Cl bond length of 2.299(1)Å are within normal ranges.[77] The

copper has a rather unusual coordination geometry, with the copper atom only 0.300(4)Å out of the coordination plane of the nitrogen and chloride atoms. This gives the complex a distorted square planar geometry, with the copper atom distorted out of the plane by an attraction to the oxygen atoms. However, the Cu-O interatomic distance [Cu1-O8 2.503(3)Å], while quite long, is within the expected bonding distance.[77]

The mononuclear $CuLCl_2$ units of **3.44** arrange with numerous C-H···Cl interactions between the hydrogen atoms of the ligand and the coordinated chloride counterions. These interactions lie in the range 2.634(4) – 2.912(4)Å and involve both methylene and aromatic hydrogen atoms. The units are also involved in π-π face-to-face interactions between the almost coplanar pyridine and benzene rings [5.6(1)°] of different molecules. The closest approach, of 3.28(1)Å, is between C5 of the pyridine ring and the plane of an adjacent benzene ring, indicating a moderately strong interaction.[9]

The structures of complexes **3.43** and **3.44** show a striking similarity to the silver nitrate and copper(II) chloride complexes of 2,3-bis(2-pyridylmethoxy)naphthalene (fig 3.37(c)). This ligand differs from **3.40** only by the replacement of the benzene for a naphthalene group. O'Keefe identified the ligand in these complexes as having tetradentate and bidentate binding modes, respectively. The differences in the bond distances between these complexes and those of **3.43** and **3.44** are small. The Ag-O distances found by O'Keefe were 2.543(3)Å and 2.545(2)Å, while the Cu···O distances are 2.521(2)Å and 2.506(2)Å.[102]

3.5.3 Coordination complexes of 3.41

The coordination chemistry of **3.41** was investigated by formation of complexes with $AgNO_3$, $CuCl_2$, $Cd(NO_3)_2$ and $ZnBr_2$. The reaction of **3.41** with silver nitrate in methanol gave a white solid, **3.47**, which analysed with an interesting M_3L_2 metal-ligand stoichiometry. Crystals suitable for X-ray crystal structure analysis were obtained by diffusion of ether into an acetonitrile solution of **3.47**.

The copper(II) chloride complex, **3.48**, was formed by the reaction of **3.41** with copper(II) chloride in methanol. The blue complex isolated analysed with a 1:1 metal-ligand stoichiometry, and was insoluble in common solvents. The analysis results are consistent with both bridging and chelating binding modes of **3.41**. No further analysis was undertaken.

The reaction of **3.41** with cadmium nitrate in methanol gave a colourless solution. This solution was allowed to slowly evaporate until colourless crystals of a cadmium nitrate

complex, **3.49**, were obtained. These crystals analysed with a 1:2 metal-ligand stoichiometry. An NMR spectrum of these crystals in methanol showed only noncoordinated ligand, possibly due to dissociation of the complex in solution. The crystals obtained from the reaction mixture were suitable for an X-ray crystal structure analysis.

The zinc bromide complex, **3.50**, was prepared by reaction with zinc bromide in methanol. This white solid analysed with a 1:1 stoichiometry, and an NMR spectrum in methanol showed only noncoordinated ligand. Single crystals suitable for X-ray structure analysis were obtained by layering a methanol solution of zinc bromide onto a dichloromethane solution of **3.41**.

Crystal structure of **3.47**

The silver nitrate complex, **3.47**, crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one silver nitrate, one molecule of **3.41** and one acetonitrile solvate molecule. This 1:1 metal-ligand stoichiometry is different from that found in the elemental analysis of crude **3.47**, and probably represents a reorganization of the structure during crystal growth in the donating solvent acetonitrile. The complex has a one-dimensional polymeric structure, with one ligand bridging two silver atoms, as shown in figure 3.40, which are separated by a distance of 11.674(2)Å. The ligand has a twisted conformation with the two pyridine groups tilted at an angle of 71.6(2)° to one another, and tilted at angles of 14.6(2)° and 64.0(2)° to the benzene ring. The silver atom has a slightly distorted linear coordination geometry with Ag-N bond lengths of 2.184(3)Å and 2.188(3)Å, and an N-Ag-N angle of 171.35(9)°.

The polymer propagates along the *b*-axis of the unit cell. The combination of the linear coordination geometry of the silver atom and the twist of the ligand combine to give the polymer an 'undulating' or 'corrugated' structure.

The silver atoms of adjacent chains are involved in weak Ag···Ag interactions, with a silver-silver distance of 3.263(3)Å. Such interactions, while weak, have been identified as structurally significant in various complexes.[22,76,127,128] The silver atoms also weakly interact with oxygen atoms of the nitrate counterions. Two of the oxygen atoms of a nitrate counterion are close to the interacting silver atoms [Ag···O 2.698(3)Å and 2.709(3)Å], so that the nitrate forms a pseudo O-N-O bridge between the silver atoms, as indicated in figure 3.41.

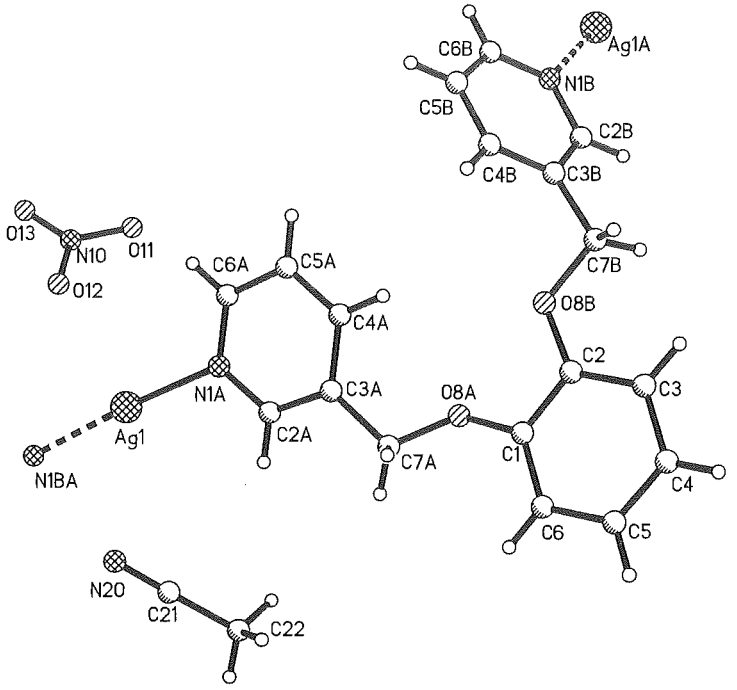


Figure 3.40 Perspective view of the structure of **3.47**, showing the asymmetric unit as part of the polymeric chain. Selected bond lengths (Å) and bond angles (°): Ag1-N1A 2.184(3), Ag1-N1BA 2.188(3), N1A-Ag1-N1BA 171.35(9).

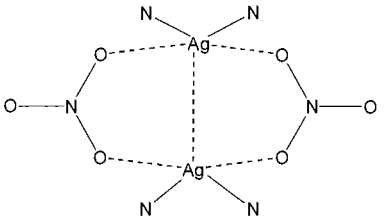


Figure 3.41 The coordination sphere of the silver atoms. The Ag···Ag and Ag···O interactions are shown as dashed lines.

The silver-silver interactions between the undulating polymer chains of **3.47** occur between alternate silver atoms. This gives the complex a pseudo two-dimensional 'brick-wall' structure, as shown in figure 3.42. The weak silver-silver interactions extend the linear silver centres into T-shaped connectors. The combination of T-shaped metal precursors and linear bridging ligands can give a variety of structures including one-dimensional ladder polymers,[129,130] two-dimensional brick walls[38,129,131] and herring-bone motifs.[83,132] A cartoon representation of this motif is shown in figure 3.43. This pseudo brick-wall structure, with Ag···Ag interactions between the polymer strands, is

similar to a silver perchlorate structure of 1,7-bis(4-pyridyl)-2,6-diazaheptane. The Ag···Ag distance in this structure is 3.18Å, indicating a slightly stronger interaction than is seen in **3.47**.[127]

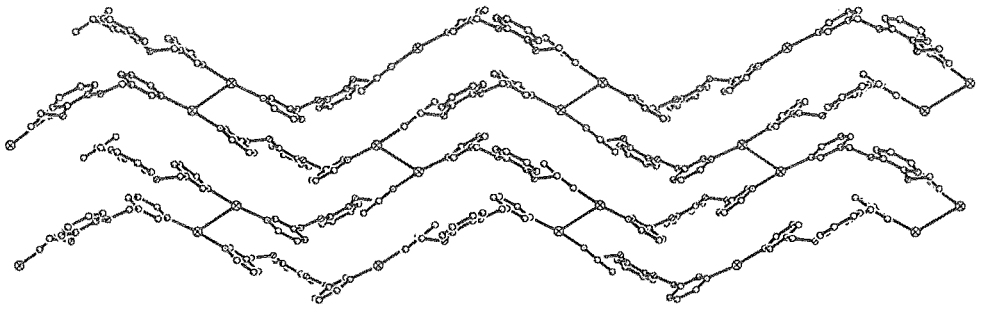


Figure 3.42 Perspective view of one layer of the pseudo two-dimensional 'brick-wall' structure of **3.47**. Hydrogen atoms and nitrate anions have been omitted for clarity.

The adjacent chains of the brick-wall polymer stack close enough to allow π-π face-to-face interactions to occur between the aromatic rings of adjacent ligands. The adjacent rings, coordinating to pairs of weakly interacting silver atoms, are almost coplanar [9.3(2)°] and slightly offset, so that C6 is 3.47(1)Å above the adjacent ring. The pyridine rings across the centre of the 'bricks', which are related by a centre of inversion, are slightly closer with the meanplanes 3.39(1)Å apart. One of the pyridine rings is also oriented towards the centre of an adjacent ring; however, the hydrogen atom is 2.95(6)Å above the ring, indicating a weak interaction only.

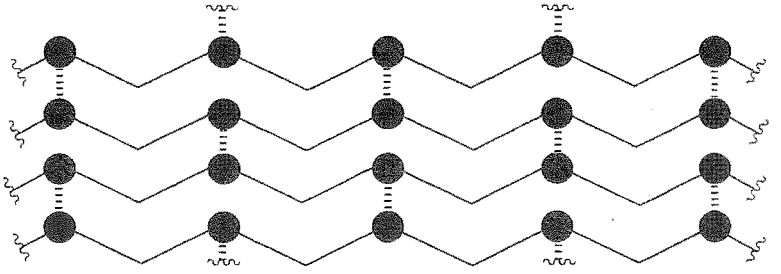


Figure 3.43 Cartoon representation of the pseudo two-dimensional 'brick-wall' structure of **3.47**. Silver-silver interactions are shown as dashed lines.

Crystal structure of 3.49

The cadmium nitrate complex, **3.49**, crystallizes in the chiral orthorhombic space group $C222_1$. The asymmetric unit contains two half molecules of **3.41**, one half cadmium nitrate, two coordinated water molecules and one water solvate molecule. The complex has a one-dimensional polymeric structure. However, only one of the molecules of **3.41** participates in the polymer, with the other being noncoordinated. Figure 3.44 shows the two independent molecules of **3.41**.

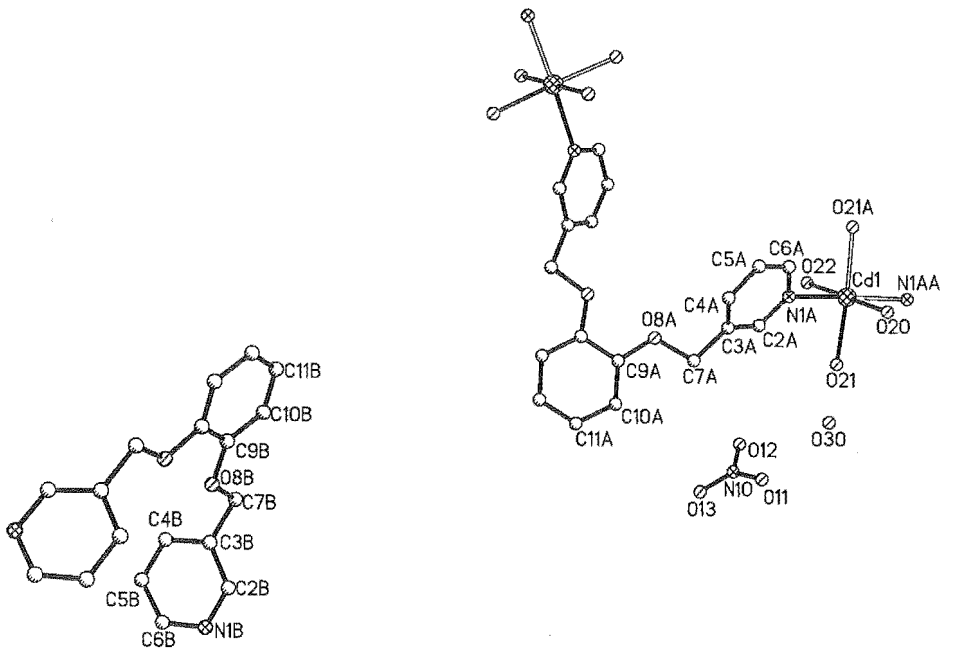


Figure 3.44 Perspective view of the structure of **3.49**, showing the two independent molecules, cadmium atoms, noncoordinated nitrate counterion and solvate water molecule. The asymmetric unit and coordination sphere of the cadmium are labelled; hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cd1-O20 2.256(3), Cd1-O21 2.293(3), Cd1-O22 2.296(3), Cd1-N1A 2.349(2), O20-Cd1-N1A 86.55(7), O21-Cd1-N1A 92.03(9), O22-Cd1-N1A 93.45(7), N1AB-Cd1-N1A 173.1(1), O21-Cd1-N1AB 88.36(9).

The structure forms with the two half molecules of **3.41** and the cadmium atom residing on two-fold rotation axes. The molecules of **3.41** both lie on two-fold rotation axes parallel to the *b*-axis, while the cadmium atoms lies on a two-fold rotation axis parallel to the *a*-axis. The molecules of **3.41** have similar conformations, with the pyridine rings tilted

at angles of 56.7(2)° and 75.1(2)° to the benzene rings for the coordinated and noncoordinated molecules, respectively. The nitrogens of the pyridine rings of both molecules are oriented away from one another, which prohibits the molecules from chelating the metal atoms. The coordinated ligand bridges two metal atoms of the helical polymer at a distance of 11.960(2)Å, a distance intriguingly similar to that found in the polymer formed by the same ligand (**3.41**) and silver nitrate (above).

The cadmium atom is coordinated by two pyridine nitrogen atoms and four oxygen atoms of water molecules. The oxygen atoms coordinate in a plane, with a two-fold axis running through the O22-Cd1-O20 atoms. The Cd-O bond distances lie in the range 2.256(2) – 2.296(2)Å. The pyridine nitrogen atoms occupy the remaining sites and are *trans* to one-another. The Cd-N bond length is 2.349(2)Å, which is slightly longer than the Cd-O bonds. This is possibly due to the increased steric bulk of the pyridine ring compared to water. The cadmium atom has a regular octahedral coordination geometry, with only slight distortions (all *cis*-angles are 90±4°). The closest cadmium atom to the pyridine nitrogen of the noncoordinated ligand is 5.038(4)Å away, and almost perpendicular to the ring, indicating no interaction.

The polymeric chains of **3.49** propagate along the *c*-axis of the unit cell. The chains stack down the *a*-axis, with the distance between cadmium atoms being 8.575(1)Å, the length of the *a*-edge of the unit cell. The noncoordinated molecules of **3.41** are sandwiched between the polymeric chains, as shown in figure 3.45. The benzene rings of the noncoordinated and coordinated molecules are almost coplanar [2.2(3)° between the meanplanes], with C10 of the noncoordinated ligand 3.66(1)Å above the plane of the coordinated molecule. This distance indicates a weak π-π face-to-face interaction. The pyridine rings of the coordinated and noncoordinated molecules are less coplanar [21.0(3)° between the meanplanes] and do not overlap, as is required for any π-π interaction. The pyridine rings of the noncoordinated molecule of **3.41** are tilted away by a hydrogen bonding interaction between N1 of the pyridine ring and the hydrogen atom of a coordinated water molecule. This interaction is moderately strong, with a D···A distance of 2.761(3)Å and θ value of 175(3)°.[4]

The nitrate anion and the solvate water molecule occupy the spaces between the polymeric chains. The nitrate anion, while not coordinated to the cadmium atom, is involved in hydrogen bonding interactions to the water molecules, both coordinated and noncoordinated. These interactions have D···A distances in the range 2.742(3) – 2.939(3)Å and θ values between 160(4)° and 175(3)°, indicating moderately strong hydrogen bonds.

All the oxygen atoms of the nitrate counterion are involved in these interactions. The solvate water molecule is hydrogen bound to one of the coordinated water molecules, with O21 being the hydrogen donor. The D···A distance is 2.656(3)Å and has an almost linear D-H···A angle [177(4)°], indicating a stronger hydrogen bond than those involving the nitrate counterion.

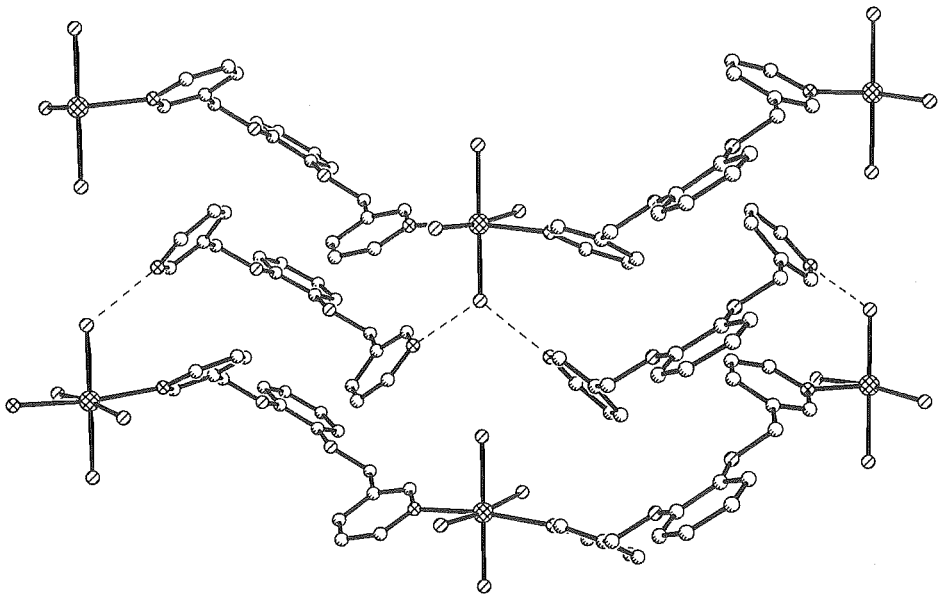


Figure 3.45 Perspective view of the stacking of the polymeric chains of **3.49**, showing the noncoordinated molecules of **3.41** sandwiched between the layers of polymer. The hydrogen bond between the noncoordinated ligand and coordinated water molecule is indicated as a dashed line between the donor (O20) and acceptor (N1B) atoms. The hydrogen atoms, noncoordinated nitrate counterion and water solvate molecule have been omitted for clarity.

The formation of helical coordination polymers has been an area of recent interest. These can be prepared from numerous structurally different starting materials. Helical polymers prepared from achiral starting materials will most commonly form in centric space groups with structures containing both right and left handed helices.[133] Spontaneous resolution into crystals containing only one enantiomer is less common.[134,135] The structure of **3.49** crystallizes in the chiral space group $C222_1$, and contains only one hand

of the helix, in this case the M-enantiomer.[‡] However, the ligand is achiral and, therefore, it is likely that the other crystals formed during the reaction are a 1:1 mixture containing either P- or M- helices. The helices propagate down the *c*-axis of the unit cell, with the units of the chains related by a two-fold screw axis. The helices have a pitch of 22.817(2)Å, shown in figure 3.46, which corresponds to the length of the *c*-edge of the unit cell.

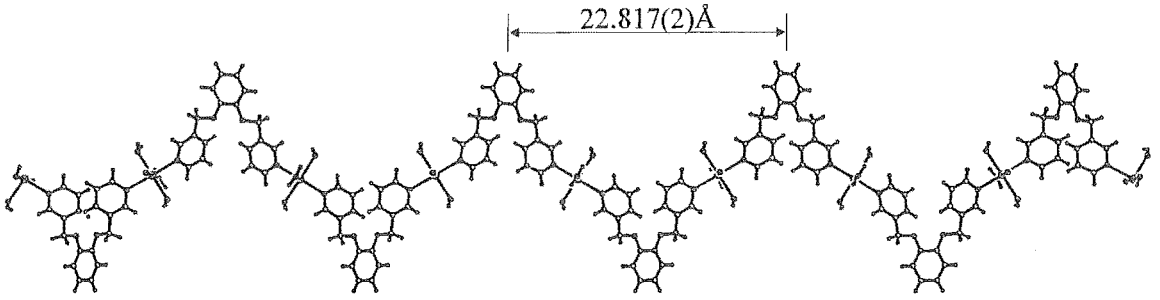
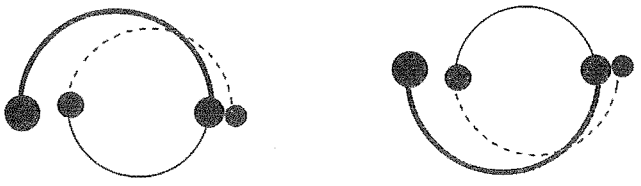


Figure 3.46 Perspective view of one of the helical chains of **3.49**. The pitch, or the distance traversed by one full 360° turn of the helix, is shown.

The absolute structure factor, or Flack x parameter, is used to ascertain if the absolute structure of a compound has been correctly determined during an X-ray structure determination.[137] During the final stages of the refinement process the value of the Flack x parameter is given with $0 \leq x \leq 1$. The determination of the absolute structure is possible if the esd of x is < 0.04, and the correct absolute structure has been determined if the value is within 3 esd's of zero.[138] The structure of **3.49** has a Flack parameter of -0.04 with an esd of 0.02, indicating that the absolute structure has been determined correctly, with the helix having M-handedness.

[‡] The chirality of a helix is defined as either M or P, where M refers to 'minus' and P to 'plus'. These designators are assigned using the CIP nomenclature,[136] with left-handed and right-handed helices having M and P chirality, respectively (shown below).



P M

Crystal structure of **3.50**

The zinc bromide complex, **3.50**, crystallizes in the triclinic space group P-1. The structure is dimeric, with one molecule of **3.41** and one zinc bromide in the asymmetric unit. The two halves of the dimer are related by a centre of inversion which lies in the middle of a 26-membered M_2L_2 macrocycle, as shown in figure 3.47. The distance between the zinc atoms across the macrocycle is 8.503(1)Å. The zinc atom is coordinated by two nitrogen atoms of the ligand (**3.41**) and two bromine atoms. The Zn-N bond lengths are 2.042(2) and 2.050(2)Å, with the Zn-Br lengths slightly longer [2.3544(7) and 2.3953(7)Å]. The zinc has a slightly distorted tetrahedral coordination geometry, with the largest angle being between the bromines [Br1-Zn-Br2 119.12(2)°].

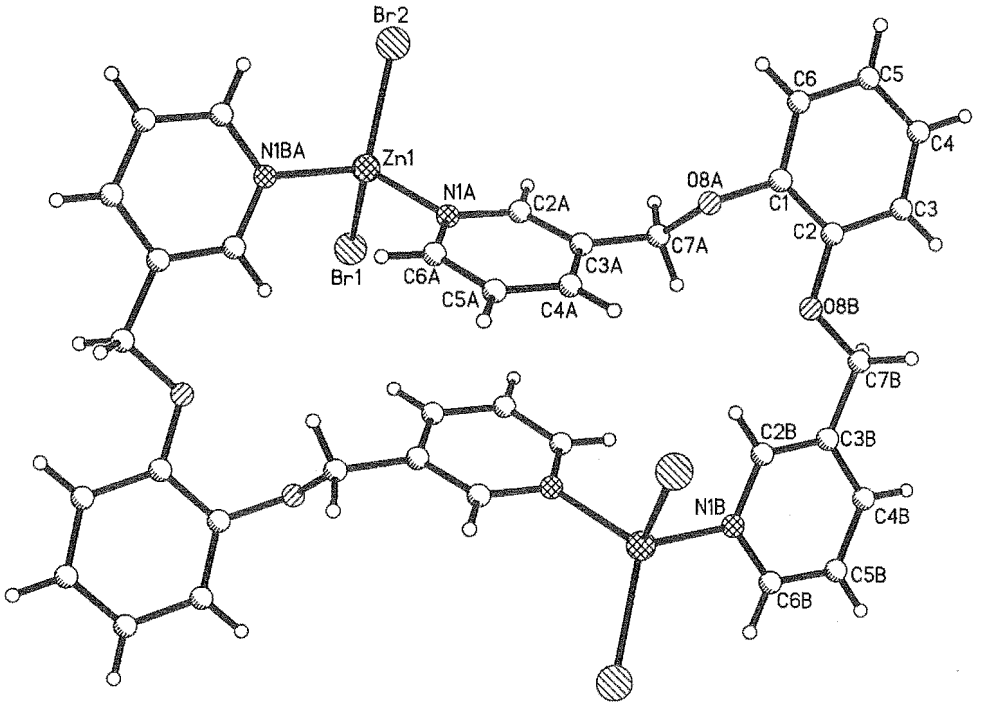


Figure 3.47 Perspective view of the M_2L_2 dimeric structure of **3.50**. Selected bond lengths (Å) and bond angles (°): Zn1-N1A 2.042(2), Zn1-N1BA 2.050(2), Zn1-Br2 2.3544(7), Zn1-Br1 2.3953(7), N1A-Zn1-N1BA 105.8(1), N1A-Zn1-Br2 111.25(7), N1A-Zn1-Br1 105.77(7), Br2-Zn1-Br1 119.12(2).

The M_2L_2 macrocycle has a rectangular appearance, with the long edge containing the coordinated zinc atoms. The short edge comprises the benzene ring and a coordinated pyridine, which are almost coplanar [9.4(1)°]. The other pyridine ring is tilted at an angle

of 60.7(1)° to the benzene ring. This pyridine ring forms a π-π face-to-face interaction with the opposite pyridine ring. These rings are related by a centre of inversion, with their meanplanes 3.471(4)Å apart.

This M_2L_2 macrocyclic structure is similar to that formed by the silver nitrate complexes of 1,4-bis(2-pyridyloxy)benzene[89] and 1,3-bis(2-pyridyloxy)benzene.[108] These complexes both form M_2L_2 macrocycles with a π-π stacking interaction. However, in these complexes this interaction occurs between the benzene rings rather than pyridine rings, as shown in figure 3.48. In the structure involving 1,4-bis(2-pyridyloxy)benzene the ligands are related by a centre of inversion, while in the structure involving 1,3-bis(2-pyridyloxy)benzene they are related by a two-fold rotation axis.

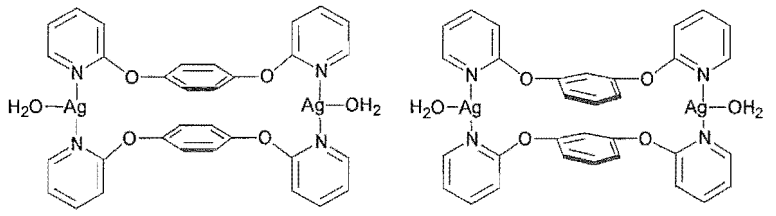
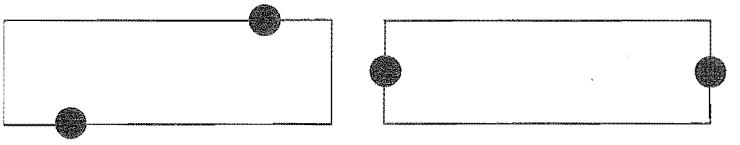


Figure 3.48 M_2L_2 structures of the silver complexes of 1,4-bis(2-pyridyloxy)benzene and 1,3-bis(2-pyridyloxy)benzene.

These complexes have structures which are topologically similar to the structure of **3.50**. All the complexes have M_2L_2 structures and π-π interactions across the macrocycles. All have a rectangular appearance. However, in the structure of **3.50** the metal atom forms part of the long side of the rectangle, with the 90° angle principally formed by the 1,2-disubstituted benzene ring. In the silver nitrate structures of 1,4-bis(2-pyridyloxy)benzene and 1,3-bis(2-pyridyloxy)benzene, the metal atom forms part of the short side of the rectangle, with the 90° angle arising from the coordination of the 2-substituted pyridine ring. These differing topologies are represented schematically in figure 3.49.



(a) (b)

Figure 3.49 A representation showing the topology of the structures described above. **(a)** **3.50**, **(b)** silver nitrate structures of 1,4-bis(2-pyridyloxy)benzene and 1,3-bis(2-pyridyloxy)benzene.

The M_2L_2 macrocyclic units of **3.50** pack with numerous interactions between them. The coordinated bromine atoms are oriented away from the macrocycle due to the tetrahedral geometry of the zinc, and these interact with the hydrogen atoms of adjacent macrocycles. The shortest of these interactions is Br1···H7AB which is 2.97(4)Å long. The macrocycles also have a methylene group which interacts with both a benzene ring and a pyridine ring of adjacent macrocycles. These interactions are both C-H···π; between H7BB and the benzene ring, and between H7BA and the pyridine ring. H7BB of the methylene ring is 2.52(4)Å directly above the centre of the benzene ring, and H7BA is 2.68(4)Å away from the centre of the N1B-C2B bond. Such interactions between non-aromatic hydrogen atoms and aromatic rings are less common than π-π interactions.[139]

3.5.4 Coordination complexes of 3.42.

The coordination chemistry of **3.42** was investigated by the formation of complexes with $AgNO_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $ZnBr_2$. The reaction of **3.42** with $AgNO_3$ gave the silver nitrate complex, **3.51**, as a brown precipitate. This precipitate analysed as [$AgNO_3$.(**3.42**)] and X-ray quality single crystals were grown by the diffusion of ether into an acetonitrile solution of **3.51**.

The copper(II) nitrate complex, **3.52**, was prepared by the reaction of **3.42** with copper(II) nitrate in methanol. The complex was isolated as small blue crystals which analysed with a 1:2 metal-ligand stoichiometry. These crystals, although well formed, were too small for X-ray structure analysis. Numerous attempts were made to grow larger crystals, but only small or severely twinned crystals could be isolated. No further analysis was undertaken.

The cadmium nitrate complex, **3.53**, was isolated from the reaction of **3.42** with cadmium nitrate in methanol. The white precipitate formed was insoluble in common solvents, and analysed as [$Cd(NO_3)_2$.(**3.42**)]. The 1:1 stoichiometry is consistent with numerous structures, including oligomeric and polymeric species. The insolubility may possibly be due to the formation of a polymeric species. No further analysis was attempted.

The reaction of **3.42** with zinc bromide in methanol gave a zinc bromide complex, **3.53**, as a white solid in good yield (75%). The complex analysed as [$ZnBr_2$.(**3.42**)] and was insoluble in common solvents. Crystals suitable for X-ray structure analysis were grown by carefully layering a solution of zinc bromide in methanol onto a solution of **3.42** in dichloromethane.

Crystal structure of **3.51**

The silver nitrate complex, **3.51**, has a one-dimensional zig-zag polymeric structure, as shown in figure 3.50. The complex crystallizes in the monoclinic space group C2/c, with half a silver nitrate and a half a molecule of **3.42** in the asymmetric unit. The silver atom lies on a centre of inversion and is coordinated by two pyridine nitrogen atoms of the ligand molecule (**3.42**). The silver atom has a strictly linear coordination geometry with identical Ag-N bond lengths of 2.151(3)Å, as a consequence of the centre of inversion.

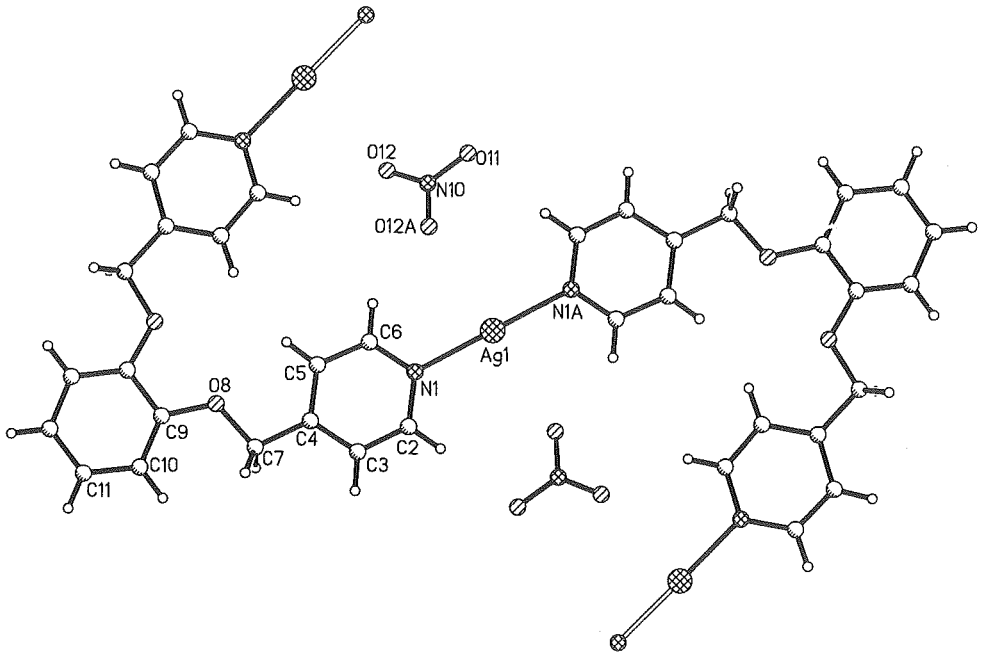


Figure 3.50 Perspective view of a section of the polymeric chain of **3.51**, with the atomic labelling shown. Selected bond length (Å): Ag1-N1 2.151(3).

The ligand molecule and nitrate counterion both lie on a two-fold axis, which relates their two halves. The polymer chains of **3.51** are remarkably planar, with the ligand having a mean deviation of only 0.052(7)Å for the meanplane of all non-hydrogen atoms. The silver atom deviates only slightly from the plane of the pyridine ring [0.011(7)Å]. The nitrate counterions are noncoordinating, with the closest approach made by O12, which is 3.037(3)Å away from the silver atom.

The polymeric chains of **3.51** are planar, and propagate along the *ac*-diagonal, with the distance between the silver atoms of the chain 7.715(2)Å. The nitrate counterions are found in the plane of the polymer, occupying the spaces between the silver atoms, as shown in figure 3.51. The planar chains stack to form a sandwich of layers, with the

polymeric chains offset so that the benzene of one chain lies above the silver atom of an adjacent chain. This offset means that the aromatic rings of the chains do not overlap, which is required for any π-π face-to-face interactions.

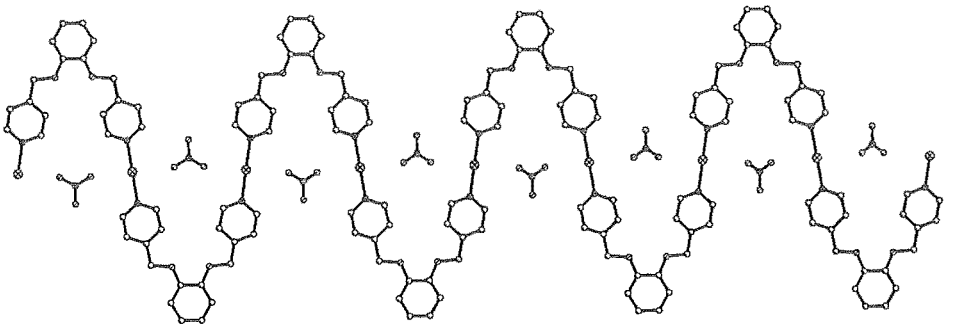


Figure 3.51 View of the zig-zag polymer of **3.51**, showing the nitrate counterions between the silver atoms. The hydrogen atoms have been omitted for clarity.

Crystal structure of **3.54**

The zinc bromide complex, **3.54**, crystallizes in the monoclinic space group $P2_1/n$, and has a one-dimensional helical polymeric structure. The asymmetric unit contains one molecule of **3.42**, one zinc bromide and partially occupied dichloromethane and methanol solvate molecules. The structure of a section of the polymer is shown in figure 3.52.

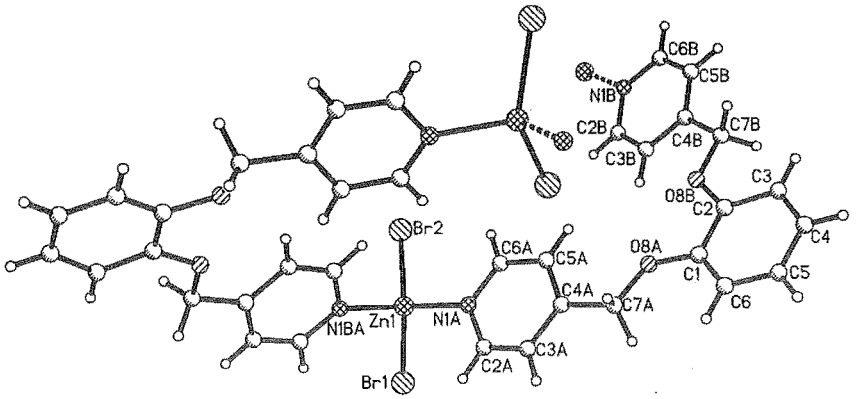


Figure 3.52 Perspective view of the helical polymer structure of **3.54** showing atomic labelling. The solvate molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1-N1BA 2.04(1), Zn1-N1A 2.04(1), Zn1-Br1 2.355(3), Zn1-Br2 2.362(3), N1BA-Zn1-N1A 104.9(5), N1BA-Zn1-Br1 106.2(4), N1A-Zn1-Br1 109.3(3), Br1-Zn1-Br2 119.5(1)

The helical polymeric strands of **3.54** are constructed from ligands which are in surprisingly similar conformations to that formed by **3.42** in the silver nitrate structure above. The ligand molecules are relatively planar, with the pyridine rings tilted slightly relative to the benzene ring, at angles of 10(2)° and 16(2)°. The zinc atom has a slightly distorted tetrahedral geometry [largest distortion 119.5(1)°], with Zn-N bond lengths of 2.04(1)Å and 2.04(1)Å. These are indistinguishable, mainly due to the poor refinement of the structure (R_1=9.60%) which increases the uncertainty of any calculated parameters.

The helical chains propagate along the *b*-axis, with the repeat units of the chain related by a two-fold screw axis. The helix has a pitch of 10.548(1)Å, which corresponds to the length of the *b*-edge of the unit cell. As stated above, the complex crystallizes in the centric monoclinic space group $P2_1/n$. The structure of **3.54** must therefore contain both P- and M-helices, related by a centre of inversion. The structure of the M-helix is shown in figure 3.53. The helices of **3.54** have large grooves, as indicated by the arrows in figure 3.53. These grooves are large enough to allow the chains of opposite chirality to form an interleaved structure, with the aromatic rings undergoing π-π face-to-face interactions. The principal interaction is between C5B and the meanplane of the benzene ring, which are 3.46(4)Å apart. The overlap only occurs between the edges of the rings due to the small size of the groove, which only permits the edges of the ligands to be interleaved.

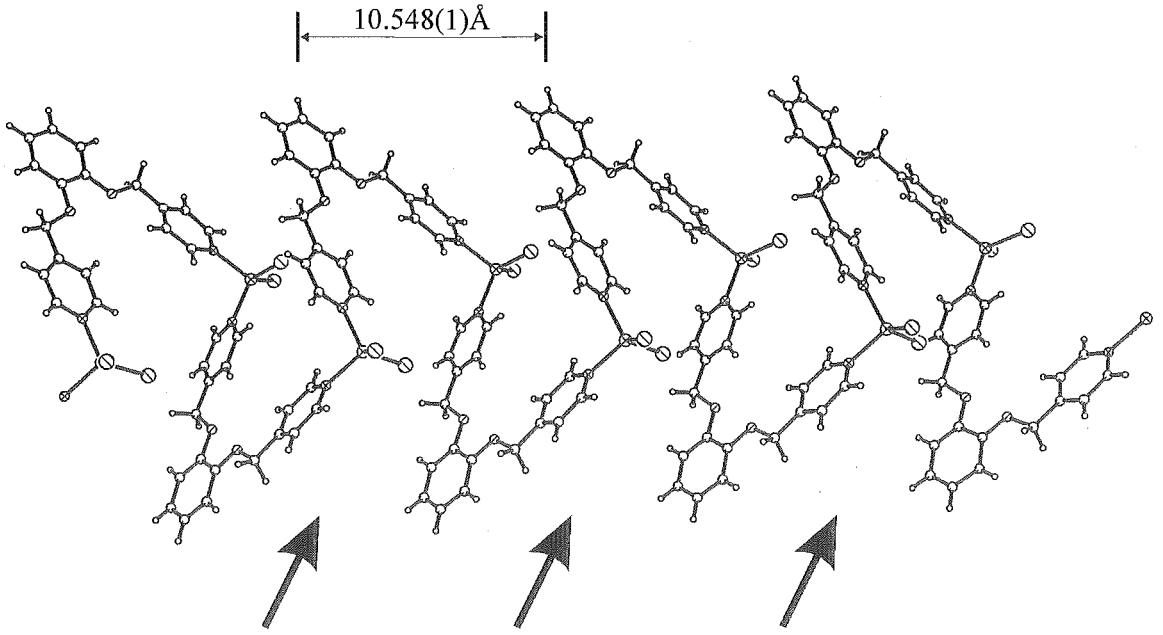
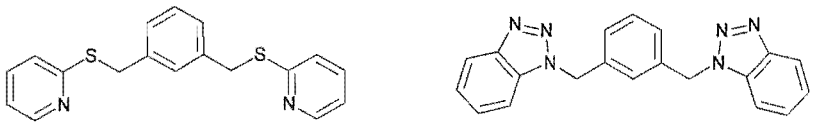


Figure 3.53 View of the helical chain structure of **3.54**, showing the pitch of the M-helix. The arrows indicate the grooves which allow interaction between chains of opposite chirality.

The complexes described above further exemplify the different possible complexes that can be formed from flexible ligands. The use of 1,2-disubstituted cores, which might be predisposed to the formation of macrocyclic complexes, has given a range of structures, including polymeric species. The ligand **3.40** forms chelating complexes with its ether oxygens interacting with the metal atoms. The ligands **3.41** and **3.42** form polymeric complexes, three of which are helical. Further interactions between the metal atoms allow the formation of a 'brickwall' type complex. The orientation of the donor atoms of **3.41** allows this molecule to form a discrete M_2L_2 macrocycle.

3.6 Resorcinol based -CH_2O- ligands

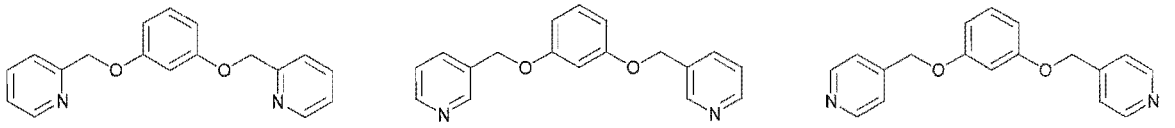
In contrast to 1,4-disubstituted aromatic rings, and to a lesser extent 1,2-disubstituted aromatic rings, flexible ligands formulated from 1,3-disubstituted aromatic cores are less common. As part of his study into various flexible ligands, Hartshorn prepared the ligand, 1,3-bis(2-pyridylsulfanylmethyl)benzene (fig 3.54(a)), which, when allowed to react with silver nitrate, gave a one-dimensional polymer.[125] The formation of discrete species with flexible ligands containing 1,3-disubstituted cores allows interesting topologies to form; for example, the formation of an M_2L_3 triple helicate using the ligand 1,3-bis(1-benzotriazolylmethyl)benzene (fig 3.54(b)) with silver nitrate.[140] The use of 1,3-disubstituted aromatic cores as part of flexible ligands as models for copper containing enzymes has shown the ability of such ligands to form discrete M_2L_2 cyclic complexes.[141]



(a) (b)

Figure 3.54

The potential ligand molecules **3.55** – **3.57** (fig 3.55) were synthesised, and their coordination chemistry investigated.

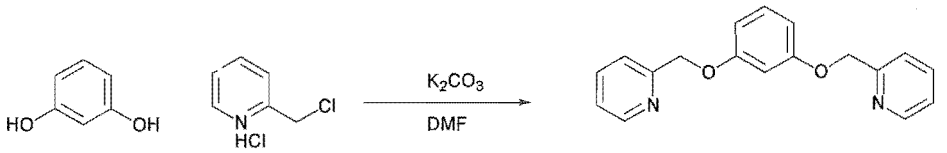


3.55 **3.56** **3.57**

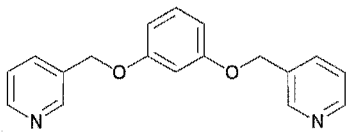
Figure 3.55

3.6.1 Ligand synthesis

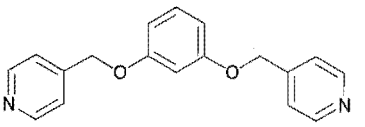
The ligands 1,3-bis(2-pyridylmethoxy)benzene (**3.55**), 1,3-bis(3-pyridylmethoxy)benzene (**3.56**) and 1,3-bis(4-pyridylmethoxy)benzene (**3.57**) were synthesised in a method analogous to that of O'Keefe, as shown in scheme 3.5. Resorcinol, two equivalents of 2-, 3- or 4-chloromethylpyridine hydrochloride and potassium carbonate were warmed in N,N-dimethylformamide. The products were purified by chromatography to give **3.55**, **3.56** and **3.57** in 75%, 43% and 40% yields, respectively. The yields for the reactions of resorcinol are higher than those using either catechol (preparations of **3.55**, **3.56** and **3.57**) or hydroquinone (preparations of **3.25** and **3.26**). This could be due to the competing oxidation of these starting materials to *o*-benzoquinone and *p*-benzoquinone, respectively.



3.55



3.56



3.57

Scheme 3.5

3.6.2 Coordination complexes of 3.55

The coordination chemistry of **3.55** was investigated by the formation of complexes with $AgNO_3$ (**3.58**), $CuCl_2$ (**3.59**), $Cd(NO_3)_2$ (**3.60**) and $ZnBr_2$ (**3.61**). The silver nitrate complex, **3.58**, was prepared by reaction of **3.55** in acetone with $AgNO_3$ in methanol. The crystals formed analysed as [$AgNO_3$.(**3.55**)] and were suitable for X-ray crystal structure analysis.

The reaction of **3.55** with $CuCl_2$ in methanol gave the copper(II) chloride complex, **3.59**, in 67% yield. The complex analysed with a 1:1 metal-ligand stoichiometry, and was insoluble in common solvents. The analysis results and general insolubility might indicate a polymeric structure. No further characterisation was carried out.

The cadmium nitrate complex, **3.60**, was prepared by the reaction of $Cd(NO_3)_2$ with **3.55** in methanol. The white crystalline complex isolated analysed as $[Cd(NO_3)_2.(\mathbf{3.55})]$, and was insoluble in common solvents. The insolubility and analysis results might indicate a polymeric structure for this complex. No further analysis was attempted.

The zinc bromide complex, **3.61**, was isolated from the reaction of **3.55** with $ZnBr_2$ in methanol. The complex analysed with a 1:1 metal-ligand stoichiometry, and was insoluble in common solvents. Single crystals suitable for X-ray structure analysis were obtained by carefully layering a methanol solution of $ZnBr_2$ onto a dichloromethane solution of **3.55**.

Crystal structure of **3.58**

The silver nitrate complex, **3.58**, crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains one molecule of **3.55** and one silver nitrate. Figure 3.56 shows the structure of **3.58**, which is a one-dimensional polymer. The silver atom is coordinated

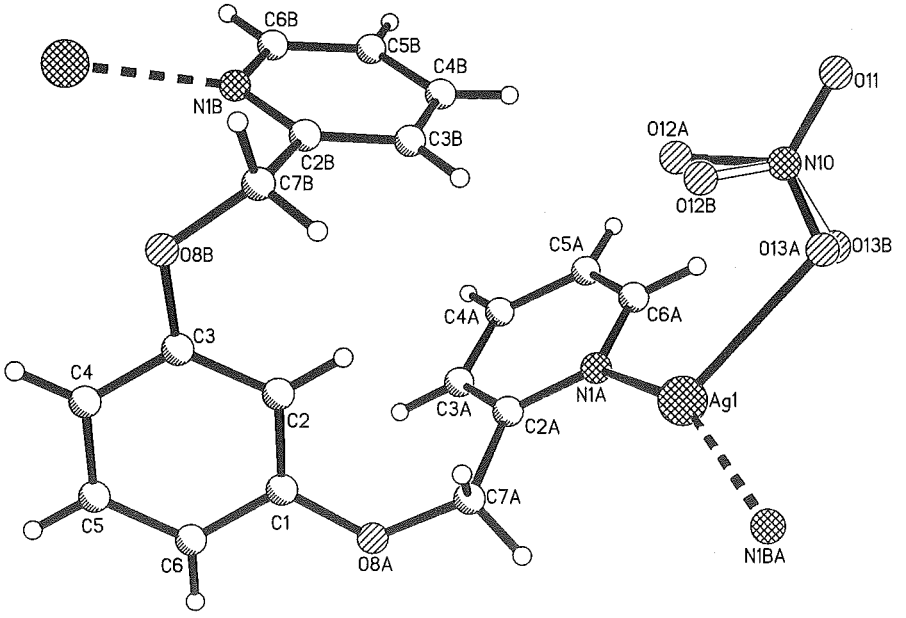


Figure 3.56 Perspective view of a section of the one-dimensional polymeric structure of **3.58**. The disordered nitrate counterion is shown with the minor coordinated component as solid bonds. Selected bond lengths (Å) and bond angles (°): Ag1-N1BA 2.205(4), Ag1-N1A 2.218(3), Ag1-O13A 2.48(2), N1B-Ag1-N1A 150.0(1), N1B-Ag1-O13A 99.2(8), N(1A)-Ag1-O13A 103(1).

by two pyridine nitrogen atoms and the oxygen atom of a nitrate anion. However, the nitrate anion is disordered over two sites, which corresponds to a 34° twist around the O11-N10 bond. As a consequence the silver atom is only coordinated by the nitrate anion 45% of the time. The Ag-N bond lengths are 2.205(4)Å and 2.218(3)Å and the Ag-O bond length is 2.48(2)Å. The silver atom has a distorted T-shaped, rather than trigonal-planar, coordination geometry, as shown by the N1B-Ag1-N1A angle of 150.0(1)°.

The ligand bridges two silver atoms, which are 8.775(2)Å apart. The pyridine rings of the ligand are oriented away from one another, and considerably tilted away from the meanplane of the benzene ring [81.0(5)° and 81.4(5)°]. This conformation allows the ligand to form a 'stepped' bridge between the two silver atoms.

The polymeric chain propagates along the *ac*-diagonal of the cell, by means of an *n*-glide plane. This symmetry relationship means that the polymer is not helical, unlike the polymeric chains of the zinc bromide complex **3.54** above. The polymeric chains interact via π-π face-to-face and edge-to-face interactions. One of the pyridine rings is related to another via a centre of inversion, which necessitates coplanarity. These pyridine rings are offset so that the C3-C4 bond lies 3.351(5)Å above the meanplane of the related pyridine ring, as shown in figure 3.57. The other pyridine ring is almost perpendicular to the benzene ring of another polymeric chain. The closest approach between these rings is made by H4 of the pyridine ring, which is 2.67(5)Å above the centre of the benzene ring, indicating a weak π-π edge-to-face interaction.

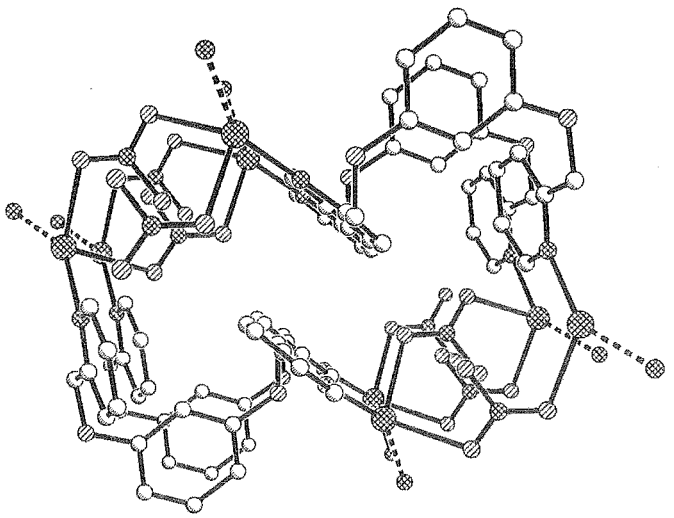


Figure 3.57 Perspective view of the structure of **3.58** looking down the *b*-axis of the unit cell, showing the π-π face-to-face interactions. The minor component of the disordered nitrate anion, which bridges the two silver atoms, is shown.

The silver atoms of the polymeric chain interact with the partially disordered nitrate anions of a neighbouring chain. This interaction occurs between the silver atoms and O11 of the nitrate anion, which has full occupancy. The Ag···O distance is 2.697(3)Å, which is slightly shorter than the interaction between the silver atom and the major component of the disordered nitrate anion [2.72(2)Å for both oxygens]. These interactions between polymer chains give the complex a pseudo two-dimensional polymeric structure.

Crystal structure of **3.61**

The zinc bromide complex, **3.61**, has a one-dimensional helical polymeric structure and crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains one molecule of **3.55**, one zinc bromide, and one water solvate molecule. The structure of **3.61** is shown in figure 3.58.

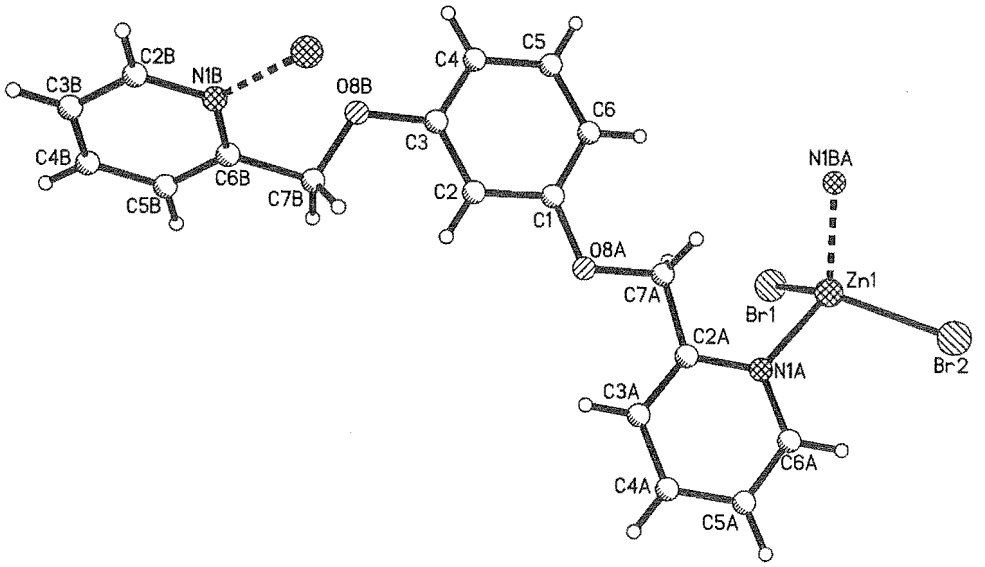


Figure 3.58 Perspective view of the helical polymeric structure of **3.61**, showing the atomic labelling. The water solvate molecule has been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn1-N1BA 2.054(5), Zn1-N1A 2.068(5), Zn1-Br2 2.361(1), Zn1-Br1 2.395(1), N1BA-Zn1-N1A 117.5(2), N1BA-Zn1-Br2 110.7(1), N1A-Zn1-Br2 107.5(1), N1BA-Zn1-Br1 102.3(1), Br2-Zn1-Br1 112.50(4).

The zinc atom is coordinated by the pyridine nitrogen atoms of two ligands and two bromine atoms, with a distorted tetrahedral geometry [largest distortion 117.5(2)°]. The

Zn-N bond lengths of 2.054(5)Å and 2.068(5)Å are similar to others seen in this work. The Zn-Br bond lengths of 2.361(1)Å and 2.395(1)Å are slightly longer. The ligand has a twisted conformation, with the pyridine rings tilted at an angle of 65.1(5)° to each other. The twist occurs to one arm of the ligand only, with the other ring almost coplanar with the benzene ring [5.2(5)°].

The polymeric chains propagate along the *b*-axis of the unit cell, with the repeat units of the chain related by a two-fold screw axis, making the polymeric chains helical. The twist of the ligand, combined with the tetrahedral geometry of the zinc atoms, gives the helical chains a pitch of 16.429(2)Å, as shown in figure 3.59. This pitch corresponds to the distance traversed by two zinc atoms and two ligands of the polymeric chain, which is the length of the *b*-edge of the unit cell. This pitch is longer than that of the zinc bromide helical polymer **3.54** (see above).

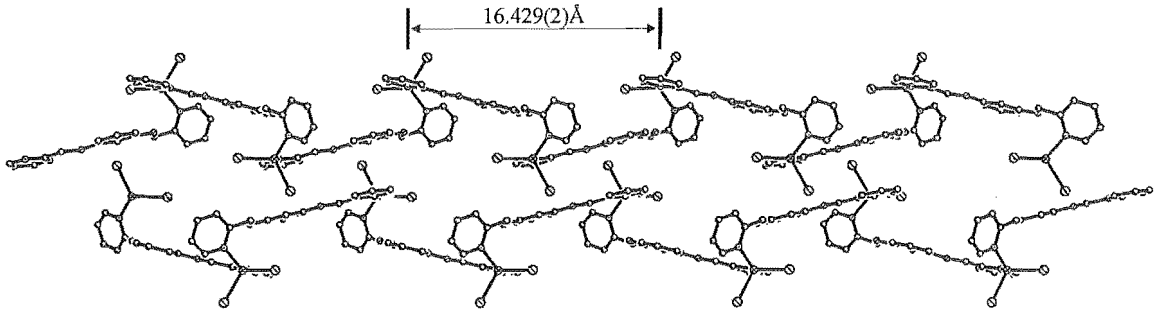


Figure 3.59 View of the two helical polymeric chains of **3.61**, related by a centre of symmetry, showing the pitch. The two chains have opposite chirality, with the top having 'P' helicity, and the bottom 'M' helicity. The π-π face-to-face interactions between opposite handed chains can be seen. Hydrogen atoms and water solvate molecules have been omitted for clarity.

The monoclinic space group $P2_1/c$ is centrosymmetric, and therefore the structure must contain both M and P handed helices, which are both shown in figure 3.59. The two chains, which are related by a centre of inversion, arrange with the long arm of the ligand molecule, comprised of the almost coplanar pyridine and benzene rings, involved in a π-π face-to-face interaction. The rings stack with the C4B-C5B bond of the pyridine ring of one chain 3.46(1)Å above the meanplane of the benzene ring of another chain. The bromine atoms interact with various hydrogens of the ligand molecule, with the closest interaction occurring between H3AA and Br2, with a distance of 2.87(4)Å.

3.6.3 Coordination complexes of 3.56

The coordination chemistry of **3.56** was investigated with the formation of complexes with $AgNO_3$, $CuCl_2$, $Cd(NO_3)_2$ and $ZnBr_2$. The silver nitrate complex, **3.62**, was prepared by the reaction of **3.56** with $AgNO_3$ in a 1:1 mixture of methanol and acetone. The small colourless crystals formed analysed with an intriguing M_4L_3 stoichiometry. Single crystals suitable for X-ray structure analysis were grown by diffusion of ether into an acetonitrile solution of **3.62**.

The copper(II) nitrate and cadmium nitrate complexes, **3.63** and **3.64**, were prepared by the reactions of **3.56** with $Cu(NO_3)_2$ and $Cd(NO_3)_2$, respectively. The complexes analysed with $[M(NO_3)_2.(\mathbf{3.56}).nH_2O]$, with M = Cu and n = ½, and M = Cd and n = 0, for the copper(II) nitrate and cadmium nitrate complexes, respectively. The complexes were both insoluble in common solvents, which, combined with the 1:1 metal-ligand stoichiometry, might possibly indicate polymeric structures for **3.63** and **3.64**. No further characterisation of either complex was undertaken.

The reaction of **3.56** with $ZnBr_2$ in methanol gave the zinc bromide complex, **3.65**, as a colourless solid. The complex was insoluble in common solvents, and analysed as $[ZnBr_2.(\mathbf{3.56})]$. The 1:1 metal-ligand stoichiometry and insolubility might indicate a polymeric structure.

Crystal structure of **3.62**

The crystals of the silver nitrate complex, **3.62**, only diffracted weakly, and the data gathered gave problems during solution and refinement (final R_1=13%). However, some structural features were noted, and are worthy of comment here. The complex has a one-dimensional polymeric structure, which crystallizes in the monoclinic space group C2/c. This 1:1 metal-ligand stoichiometry is not the same as that of the small colourless crystals isolated above. This is probably due to a reorganization of the complex during crystal growth. No crystals suitable for X-ray structure analysis with the 4:3 metal-ligand ratio could be isolated. The asymmetric unit contains one ligand, one silver nitrate, and a water solvate molecule. The structure of **3.62** is shown in figure 3.60.

The silver atom is coordinated by two pyridine nitrogen atoms and a water molecule. The three coordinate silver atom has a distorted T-shaped coordination geometry, with Ag-N bond lengths of 2.17(2)Å and 2.18(2)Å. The Ag-O bond length is longer [2.52(4)Å], and this water molecule appears to be only partially occupied, with this site occupied approximately 40% of the time. Due to the poor quality of the crystal, and problems with

the collected data, these values have high esd's, making a more accurate description unreasonable.

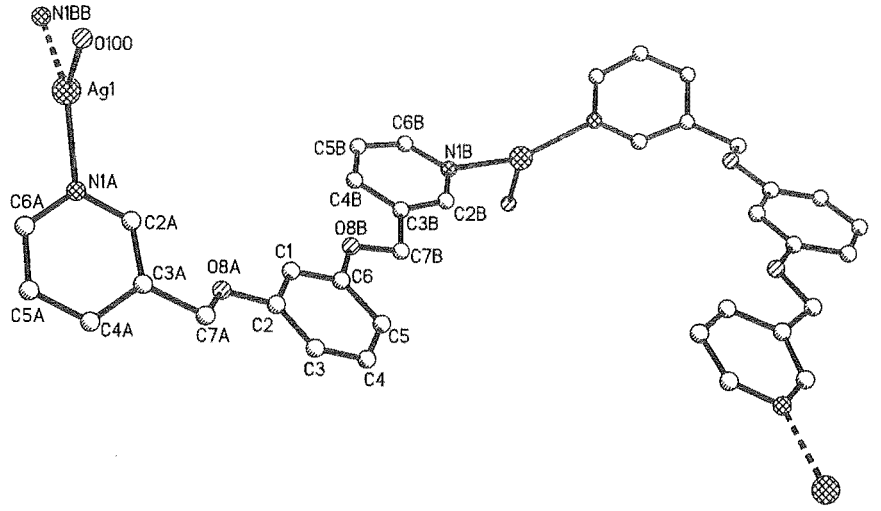


Figure 3.60 Perspective view of the polymeric structure of **3.62**, showing the atomic labelling. The disordered nitrate counterions have been omitted for clarity. Selected bond lengths (Å) and bond angles (°) Ag1-N1A 2.17(2), Ag1-N1BB 2.18(2), Ag1-O100 2.52(4), N1A-Ag1-N1BB 151.8(6), N1A-Ag1-O100 100.2(8), N1BB-Ag1-O100 107.4(8)

The polymeric chains propagate along the *b*-axis of the unit cell and are helical. Each chain is intertwined with a chain of the same chirality, with the pairs related to one another by the two-fold axis, giving the structure a 'double' helix topology. The chains have a pitch of 18.136(2)Å, which is twice the length of the *b*-edge of the unit cell. The intertwined chains form a π-π stack, with face-to-face interactions between a pyridine ring and an almost coplanar benzene ring [13(3)°]. The closest interaction occurs between the centroid of the pyridine ring, which is 3.6(5)Å above the centroid of the benzene ring.

3.6.4 Coordination complexes of 3.57

The coordination chemistry of **3.57** was investigated by the formation of complexes with $AgNO_3$ (**3.66**), $CuCl_2$ (**3.67**), $Cd(NO_3)_2$ (**3.68**), and $ZnBr_2$ (**3.69**). The reaction of **3.57** with silver nitrate in methanol gave **3.66** as a light brown precipitate. This precipitate analysed as [$AgNO_3$.(**3.57**)]. Numerous attempts to form crystals suitable for X-ray structure determination were undertaken, but all attempts isolated only small needle-like crystals. No further analysis was undertaken.

The copper(II) chloride complex, **3.67**, was isolated from the reaction of **3.57** with $CuCl_2$ in methanol. The blue complex analysed as [$CuCl_2$.(**3.57**)], and was insoluble in common solvents. The insolubility and analysis results could indicate a polymeric structure for the complex. No further characterisation was carried out.

The cadmium nitrate complex, **3.68**, was prepared by the reaction of **3.57** with cadmium nitrate in methanol. The large block-like crystals isolated analysed as [$Cd(NO_3)_2$.(**3.57**)$_2$.H_2O], and were insoluble in common solvents. The crystals isolated from the reaction mixture were suitable for X-ray crystal structure analysis.

The reaction of **3.57** with $ZnBr_2$ in methanol gave the zinc bromide complex, **3.69**, in 64% yield as a white crystalline solid. The complex analysed with a 1:1 metal-ligand stoichiometry. The complex was soluble in DMSO, however, an NMR analysis showed only noncoordinated ligand. No further characterisation was undertaken.

Crystal structure of **3.68**

The cadmium nitrate complex, **3.68**, crystallizes in the orthorhombic space group Pnma. The data collected proved to be problematic, and the structure found refined poorly (R_1=9.9%). The complex has a polymeric structure, with an asymmetric unit containing two separate half molecules of **3.57**, half a cadmium nitrate, and half a water molecule. The complex has a one-dimensional polymeric structure and, like the cadmium nitrate complex **3.49** above, has one molecule of **3.57** coordinated to cadmium atoms and one molecule noncoordinated. The structure of **3.68** is shown in figure 3.61.

The cadmium atom lies on a mirror plane, which also bisects both nitrate anions and the coordinated water molecule. The cadmium atom is coordinated by the nitrogen atoms of two ligand molecules and the oxygen atoms of one water molecule, and two nitrate anions which are both chelating. The Cd-N bond length is 2.325(6)Å, and the cadmium-water bond length is 2.271(8)Å, which is shorter than the Cd-O bond lengths for the chelating nitrate anions [Cd1-O11 2.52(1)Å and Cd1-O21 2.542(9)Å]. The nitrate anions chelate the cadmium atom symmetrically due to the bisecting mirror plane. The cadmium atom also interacts with the noncoordinated oxygen atom of a nitrate anion of an adjacent chain, with a Cd-O distance of 2.80(1)Å. This makes the complex pseudo-octacoordinate, with the nitrogen atoms trans to one another [N1A-Cd-N1AB 140.3(4)°]. The coordinated and noncoordinated molecules of **3.57** are in similar conformations, with the pyridine rings tilted at angles of 19(1)° and 23(1)° to the benzene rings, respectively.

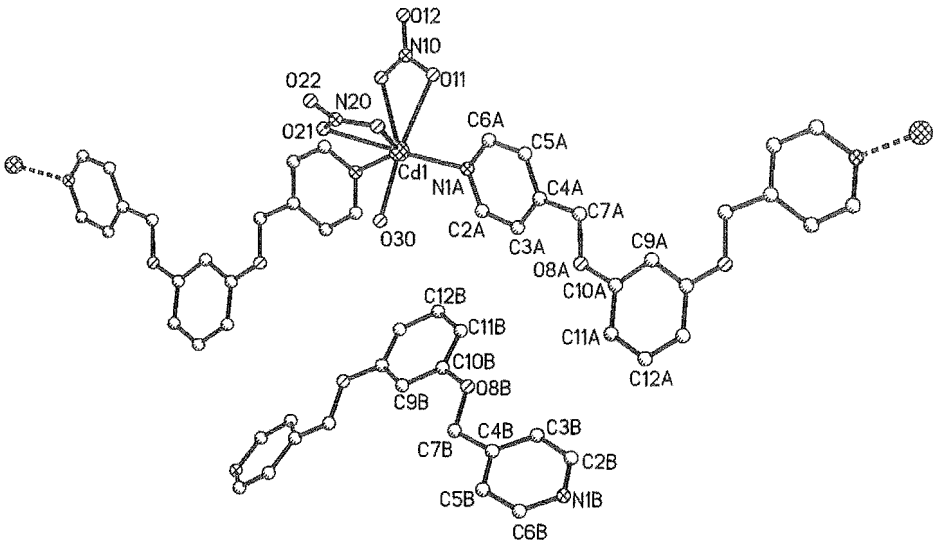


Figure 3.61 Perspective view of the two independent molecules of **3.57** in the cadmium nitrate complex **3.68** with the asymmetric unit labelled. Selected bond lengths (Å) and bond angles (°): Cd1-O30 2.271(8), Cd1-N1A 2.325(6), Cd1-O11 2.52(1), Cd1-O21 2.542(9), O30-Cd1-N1A 82.4(2), N1A-Cd1-O11 78.8(2), O30-Cd1-O11 152.7(2), O30-Cd1-O21 83.8(3), O11-Cd1-O21 93.7(3), N1A-Cd1-O21 131.0(2).

The polymeric chains propagate along the *b*-axis of the unit cell, with the cadmium atoms of the polymer 17.411(5)Å apart. The chains stack with noncoordinated molecules of **3.57** sandwiched between polymeric layers. The aromatic rings of the noncoordinated molecules of **3.57** are involved in π-π interactions with the adjacent coordinated molecules of **3.57**. These interactions are quite weak, with only the edges of adjacent molecules overlapped. The pyridine ring is hydrogen bonded to the coordinated water molecule, with a D···A distance of 2.744(8)Å and an θ value of 164(9)°, indicating a moderately strong hydrogen bond. The interactions of the nitrate anions between adjacent cadmium atoms bridge the layers along the *c*-axis of the unit cell, giving a pseudo two-dimensional polymeric structure.

This structure is remarkably similar to the cadmium nitrate complex of **3.41**. Both these structures are polymeric, with one chiral (**3.49**) and the other achiral (**3.68**). The structures contain a 1:1 mixture of coordinated and noncoordinated molecules of **3.41** and **3.57**, respectively. In each case the noncoordinated molecules are sandwiched between layers of polymeric chains. These noncoordinated ligands are held in this layer formation

via weak π-π interactions between overlapped adjacent rings and moderately strong hydrogen bonds between the pyridine nitrogen atoms and coordinated water molecules. This represents a remarkable selectivity for the different, yet structurally similar, ligands, **3.41** and **3.57**. The formation of complexes with noncoordinated ligand hydrogen-bound to coordinated water molecules has been observed for complexes of other flexible ligands, such as the $Cd(ClO_4)_2$ and $Ni(NO_3)_2$ complexes of 1,3-bis(4-pyridyl)propane.[79,142] The formation of these layered compounds may be due to the ability of the flexible molecules to arrange in conformations which allow such interactions to occur.

3.7 Phloroglucinol based -CH_2O- ligands

Flexible ligands with trisubstituted benzene rings have been used in the formation of various discrete cage-like structures, as discussed in the introduction. The increase in the number of possible donor atoms from two to three allows the formulation of closed cage structures, when combined with metal precursors. Reaction of ligands such as 1,3,5-tris(4-pyridylmethyl)benzene (fig 3.62) with metal atoms in the presence of selected host molecules induces the formation of cage-like structures.[143] Interestingly, flexible ligands with trisubstituted benzene cores have not found extensive use in the formation of polymeric compounds.

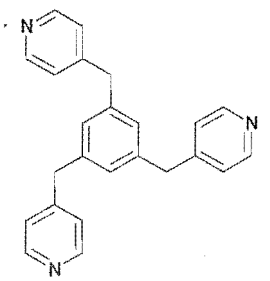
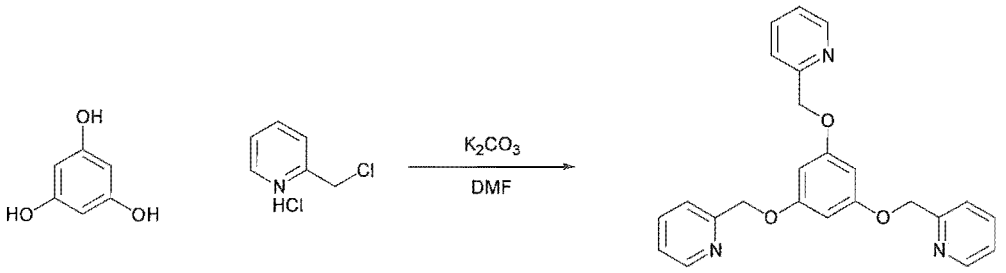


Figure 3.62

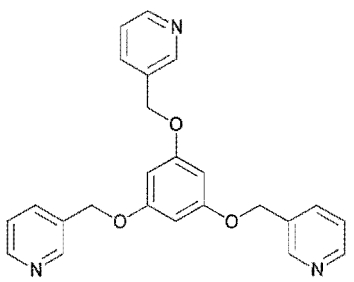
3.7.1 Ligand synthesis

The ligands 1,3,5-tris(2-pyridylmethoxy)benzene (**3.70**), 1,3,5-tris(3-pyridylmethoxy)-benzene (**3.71**) and 1,3,5-tris(4-pyridylmethoxy)benzene (**3.72**) were synthesised using a method similar to the method of O'Keefe used above. Phloroglucinol, or phloroglucinol

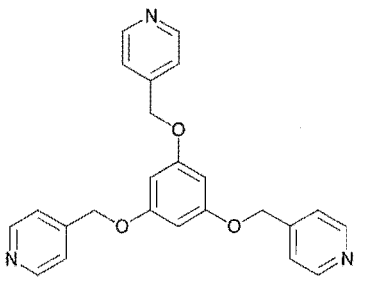
dihydrate, was warmed in N,N-dimethylformamide with 2-, 3- or 4-chloromethylpyridine hydrochloride and potassium carbonate, as shown in scheme 3.6. The resulting products, **3.70**, **3.71** and **3.72**, were purified by column chromatography and recrystallization, and were isolated as white solids in 39%, 36% and 39% yields, respectively. The compounds were characterised by melting point, elemental and mass spectrographic analysis and NMR spectroscopy.



3.70



3.71



3.72

Scheme 3.6

3.7.2 Coordination complexes of 3.70

The coordination chemistry of **3.70** was investigated by the preparation of complexes with $AgNO_3$ (**3.73**), $CuCl_2$ (**3.74**), $Cd(NO_3)$ (**3.75**) and $ZnBr_2$ (**3.76**). The reaction of **3.70** in acetone with silver nitrate in methanol gave the silver nitrate complex, **3.73**, as a white precipitate in excellent yield (98%). This solid analysed with a 2:1 metal-ligand stoichiometry. Crystals suitable for X-ray single crystal structure analysis were grown by diffusion of pentane into an acetonitrile solution of **3.73**.

The copper(II) chloride complex, **3.74**, was prepared by carefully layering a methanol solution of $CuCl_2$ onto a dichloromethane solution of **3.70**. The block-like blue-green crystals formed analysed with an interesting M_3L_2 stoichiometry. This 3:2 metal-ligand

ratio could indicate various species including M_6L_4 cage-like structures, with the copper atoms as linear bridges and the ligands tridentate. The palladium chloride complex of the structurally similar ligand 1,3,5-tris(1-pyrazolylmethyl)-2,4,6-triethylbenzene (fig 3.5) has this structural motif, and forms a 10-membered cage with $PdCl_2$, that encapsulates a DMSO solvate molecule.[28] The crystals of **3.74** obtained from the initial layering reaction were suitable for X-ray structural analysis.

The reaction of **3.70** with cadmium nitrate in methanol gave a colourless solution. A white crystalline powder was obtained by reduction of the solvent followed by diffusion of ether into the solution. The powder analysed with a 3:1 metal-ligand stoichiometry. An NMR spectrum of the complex showed only noncoordinated **3.70**. No further analysis was undertaken.

The zinc bromide complex, **3.76**, was prepared by carefully layering a methanol solution of $ZnBr_2$ onto a dichloromethane solution of **3.70**. The colourless crystals formed analysed as [$ZnBr_2$.(**3.70**)]. The complex was soluble in acetonitrile, however, an NMR study showed only noncoordinated ligand. The crystals obtained from the layering were suitable for X-ray structure analysis.

Crystal structure of **3.73**

The silver nitrate complex, **3.73**, crystallizes in the triclinic space group P-1. The asymmetric unit contains one molecule of **3.70** and two silver nitrates. The complex has a macrocyclic structure, as shown in figure 3.63.

The macrocyclic structure consists of two molecules of **3.70** which are bridged by two silver atoms, giving a 24-membered dimetallomacrocycle. The remaining pyridine ring of the ligand molecule is coordinated to another silver atom. The silver atoms which are part of the 24-membered macrocycle have a slightly distorted linear coordination geometry, with Ag-N bond lengths of 2.188(3)Å and 2.189(3)Å. The remaining silver atom is coordinated by one pyridine, with an Ag-N bond length of 2.218(3)Å, and three oxygen atoms of two nitrate anions. One of the nitrate anions chelates the silver through two oxygen atoms with bond lengths 2.459(3) and 2.573(3)Å, while the other is monodentate with an Ag-O bond length of 2.347(3)Å.

The pyridine rings of the ligand molecules are slightly tilted relative to the central benzene ring at angles of 23.9(7)°, 18.4(7)°, and 40.7(7)°. These, combined with the flexibility of the spacer groups, allow the ligands to form a macrocyclic structure with the remaining pyridine rings pointed in opposite directions, or *anti* to one another. The

macrocycle forms with a centre of inversion in the middle, making the opposite benzene rings necessarily coplanar. These rings overlap, with the centre of the C1-C2 bond 3.49(1)Å above the adjacent ring.

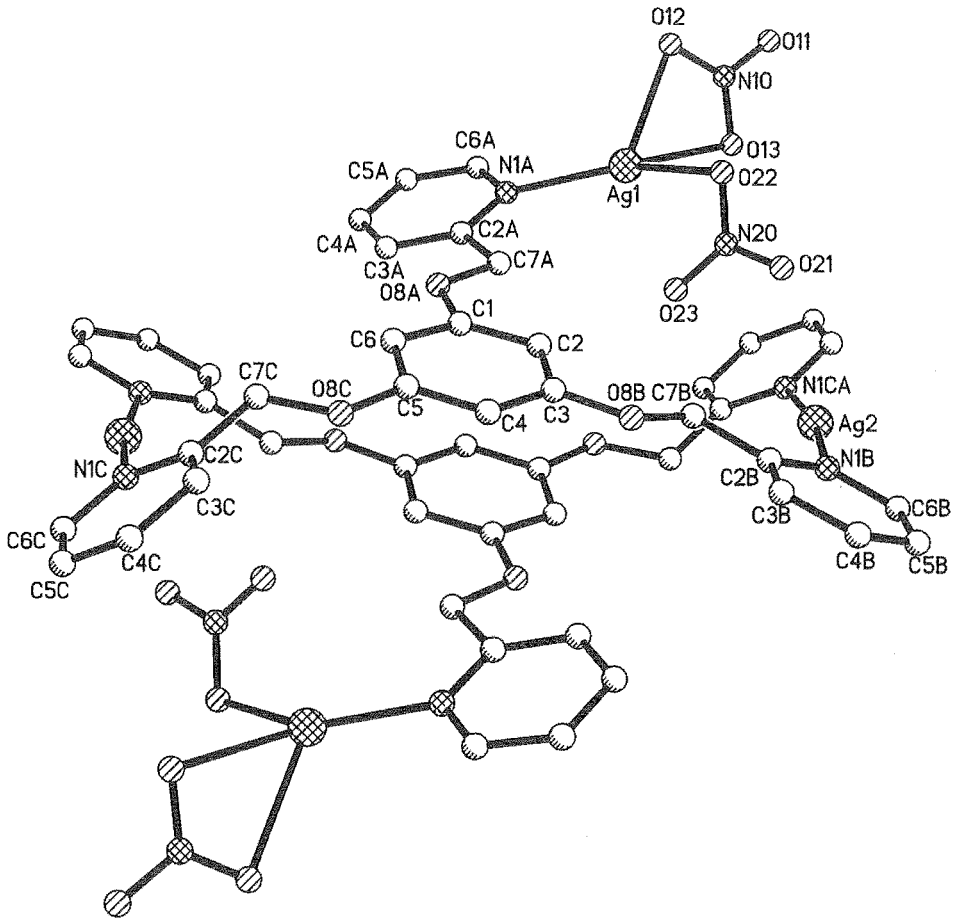


Figure 3.63 Perspective view of the macrocyclic structure of **3.73**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N1A 2.218(3), Ag1-O22 2.347(3), Ag1-O13 2.459(3), Ag1-O12 2.573(3), Ag2-N1B 2.188(3), Ag2-N1CA 2.189(3), N1A-Ag1-O22 142.2(1), N1A-Ag1-O13 133.3(1), O22-Ag1-O13 82.9(1), N1A-Ag1-O12 113.60(9), O22-Ag1-O12 97.6(1), N1B-Ag2-N1CA 170.6(1).

The macrocyclic units pack with numerous interactions between adjacent units. The benzene cores arrange with the edges overlapped and 3.385(5)Å apart, indicating a π-π interaction. The noncoordinated oxygen atom of the chelating nitrate anion interacts with the bridging silver atom [Ag···O 2.727(3)Å], and this interaction distorts the silver atom from a linear geometry. The noncoordinated oxygen atoms of the nitrate anions also

interact with numerous hydrogen atoms, the closest of which has a O···H distance of 2.30(5)Å.

Crystal structure of **3.74**

The copper(II) chloride complex, **3.74**, crystallizes in the monoclinic space group C2/m. The structure is highly disordered and could only be refined to give an R_1 value of 8.5%. The asymmetric unit contains half a molecule of **3.70**, three quarters of a copper(II) chloride and some disordered water solvate molecules, which is equivalent to the M_3L_2 stoichiometry found in the elemental analysis. The complex has a two-dimensional polymeric structure, with the ligand coordinated to three copper atoms, as shown in figure 3.64.

The ligand lies on a mirror plane, which bisects the benzene ring through C1 and C4. One of the pyridine arms of the ligand is disordered between two sites on opposite sides of Cu1; the rings are related by a mirror plane. The disordered pyridine ring is rather nonplanar, with a mean deviation of 0.060Å for the non-hydrogen atoms; this is in contrast to the fully occupied and ordered pyridine ring which has a mean deviation of 0.015Å. The bond lengths of the disordered pyridine rings lie in the range 0.97(5) – 1.77(7)Å, with an average bond length of 1.37Å. The disordered pyridine ring is almost perpendicular to the central benzene ring, tilted at an angle of 87.1(3)°.

The copper atoms of the structure both lie on special positions. Cu2 lies on an inversion centre, while Cu1 has coordinates 0,½,½, which, therefore, lies on both the mirror plane and the two-fold rotation axis. The ligand chelates the copper atoms through a pyridine nitrogen and ether oxygen to give a 5-membered chelate ring. Both the copper atoms are chelated by two different ligands and coordinated by two chlorine atoms. Cu2 has a Cu-N bond length of 2.003(6)Å, a Cu-Cl bond length of 2.297(3)Å and a Cu-O bond length of 2.530(5)Å. Cu1 has a Cu-Cl bond length of 2.277(3)Å and a Cu-O bond length of 2.605(5)Å. The Cu1-N1A bond length of 2.00(2)Å is less accurate due to the disorder of the pyridine ring. The copper atoms both have an octahedral geometry, with angles distorted by the O,N chelate ring of the ligand [chelate ring angles of 74.5(4)° and 70.6(2)°]. The octahedral geometry of the copper atoms is also subject to Jahn-Teller distortions, with the Cu-O bonds significantly longer than the Cu-N and Cu-Cl bonds. The apical Cu-O bonds and equatorial Cu-N and Cu-Cl bond lengths are within the range for hexacoordinate polymeric complexes involving copper(II).[144]

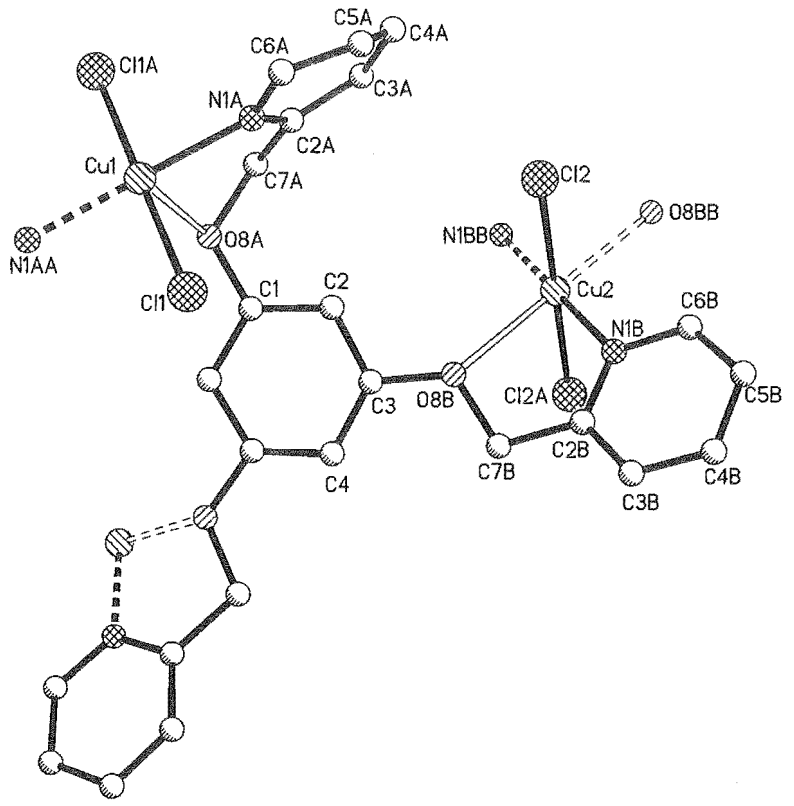


Figure 3.64 Perspective view of a section of the two-dimensional polymeric structure of **3.74**, showing one of the disordered 2-pyridylmethyl substitutents (N1A-C7A). The hydrogen atoms and solvate water molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1A 2.00(2), Cu1-Cl1 2.277(3), Cu1-O8A 2.605(7), Cu2-N1B 2.003(6), Cu2-Cl2 2.297(3), Cu2-O8B 2.530(5), N1A-Cu1-Cl1 97.4(4), N1A-Cu1-O8A 74.5(4), Cl1-Cu1-O8A 93.6(2), N1B-Cu2-Cl2 90.4(2), N1B-Cu2-O8B 70.6(2), Cl2-Cu2-O8B 92.1(2).

The two-dimensional polymeric structure of **3.74** extends in a sheet parallel to the *ab*-plane of the unit cell. The structure has a [6,3]-net topology,[18,145] with each of the tridentate ligands attached to three other ligands by bridging copper atoms. The honeycomb [6,3]-net type structure has been observed with organic compounds such as trimesic acid, with the units linked via hydrogen bonds.[146] Coordination compounds with this structure have been described involving various tridentate ligands. The silver triflate structure with 1,3,5-tricyanobenzene forms a planar [6,3]-net,[147] while less planar ligands such as hexamine form undulating nets with various metals.[148] These structures involve tridentate ligands and trigonal metals atoms, while the structure of **3.74** involves tridentate

ligands and linear metal connectors. A cartoon representation of the structure is shown in figure 3.65.

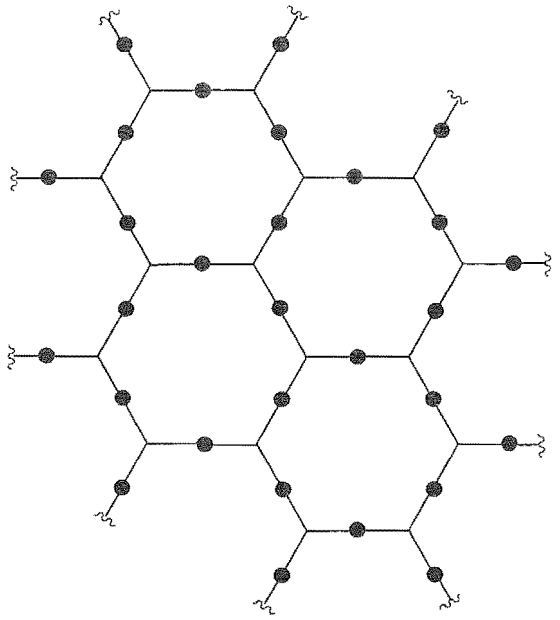


Figure 3.65 Cartoon representation of the honeycomb [6,3]-net topology of the structure of **3.74**.

The honeycomb structure has large M_6L_6 macrocycles, which are made up from four Cu2 atoms and two Cu1 atoms. The macrocycles surround large cavities, which contain the disordered dichloromethane solvate molecules. The poorly defined nature of the structure makes the location and accurate description of the solvate molecules impossible.

Crystal structure of **3.76**

The zinc bromide complex, **3.76**, crystallizes in the triclinic space group P-1. The asymmetric unit contains one molecule of **3.70**, one zinc bromide and one partially occupied water solvate molecule. The complex forms an M_2L_2 macrocyclic structure, as shown in figure 3.66. The ligand is bidentate, with a pendant pyridine arm that is disordered over two sites, with the major component having 60% occupancy. A water solvate molecule shares occupancy with the minor component, however, it is present only 40% of the time, 20% less than is possible.

The zinc atom is coordinated by the pyridine nitrogen atoms of two ligands and by two bromine atoms, and has a slightly distorted tetrahedral coordination environment. The Zn-N bond lengths, 2.094(3)Å and 2.064(3)Å, are slightly shorter than the Zn-Br bond

lengths of 2.380(1) and 2.413(1)Å. The coordinated pyridine rings of the ligand are tilted at angles of 15.2(2)° and 76.4(2)° to the benzene ring, which, combined with the tetrahedral zinc, allows a macrocyclic structure to form. The disordered pyridine rings are almost perpendicular to the central benzene ring, with angles of 80.8(3)° and 85.6(3)° for the major and minor components, respectively.

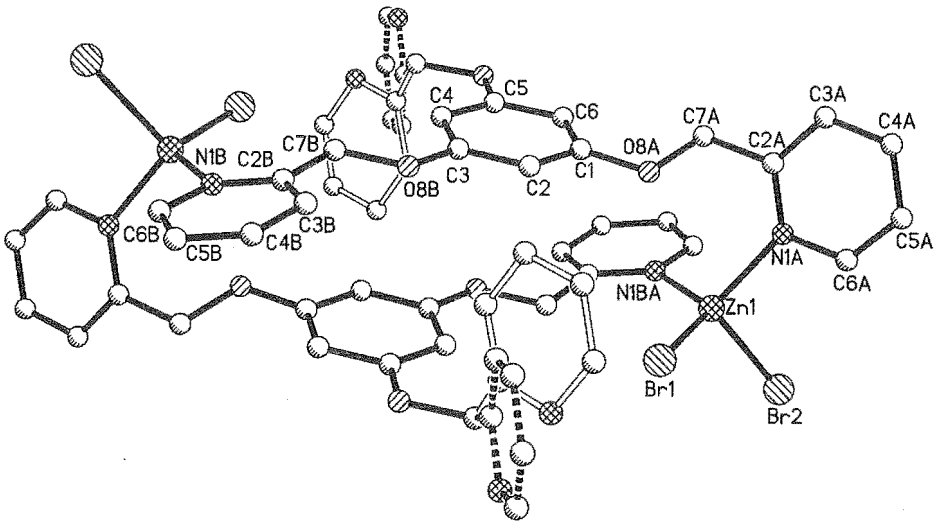


Figure 3.66 Perspective view of the macrocyclic structure of **3.76.** The disordered pyridine arms are shown with the major component as dashed bonds and the minor component as hollow bonds. The hydrogen atoms and solvate water molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn1-N1A 2.064(3), Zn1-N1BA 2.094(3), Zn1-Br1 2.380(1), Zn1-Br2 2.413(1), N1A-Zn1-N1BA 110.8(1), N1A-Zn1-Br1 105.99(9), N1BA-Zn1-Br1 123.67(9), N1A-Zn1-Br2 104.91(9), N1BA-Zn1-Br2 98.06(9), Br1-Zn1-Br2 111.93(4).

The M_2L_2 macrocycle has a similar topology to the zinc bromide complex **3.50** (above). The 24-membered macrocycle forms about a centre of inversion that relates the two halves, with the Zn···Zn distance across the macrocycle being 10.792(1)Å. However, unlike the structure of **3.50**, there is no π-π interaction between the central benzene cores, as the ligands are offset so that the benzene rings do not overlap. In the structure of **3.50** above, the angle of the macrocycles is made by a 1,2-disubstituted benzene. In the structure of **3.76** the angle of the macrocycle is made by a 2-substituted pyridine ring. This is similar to the silver nitrate structures of 1,4-bis(2-pyridyloxy)benzene and 1,3-bis(2-

pyridyloxy)benzene described above. However, the zinc atom in the structure of **3.76** is part of the long side of the rectangular structure, similar to the structure of **3.50**.

The M_2L_2 macrocyclic units of **3.76** pack in the crystal with the benzene rings of two adjacent macrocycles related by a centre of inversion. One of the carbon atoms of the coplanar benzene rings overlaps another, with the atoms 3.42(1)Å apart, indicating a weak π-π interaction.

This structure is similar to that formed by O'Keefe from the potential ligand 2,3,6,7,10,11-hexakis(2-pyridyloxy)triphenylene (fig 3.67). When this ligand is allowed to react with copper(II) chloride, an M_2L_2 complex is isolated. This complex has a macrocyclic structure, with only two of the pyridine rings of each ligand coordinated to the copper atoms. The remaining rings are noncoordinating, and one is disordered over three sites. The triphenylene cores of the two ligands are involved in π-π face-to-face interactions.[102]

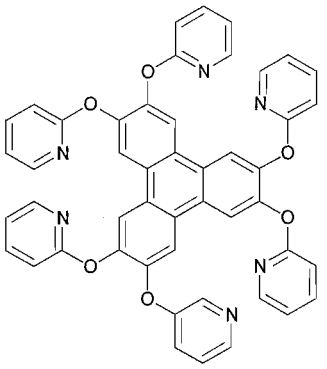


Figure 3.67

3.7.3 Coordination complexes of 3.71.

The coordination chemistry of **3.71** was investigated by formation of complexes with $AgBF_4$ (**3.77**), $Cu(NO_3)_2$ (**3.78**), $Cd(NO_3)_2$ (**3.79**) and $ZnBr_2$ (**3.80**). The silver tetrafluoroborate complex, **3.77**, was prepared by diffusion of pentane into an acetonitrile solution containing **3.71** and silver tetrafluoroborate. The colourless crystals collected analysed with an interesting M_3L_2 stoichiometry. This could indicate various interesting cage-like structures involving linear bridging silver atoms and tridentate ligands, as outlined for the copper(II) chloride complex (**3.74**), which has a similar stoichiometry. The crystals obtained via diffusion of pentane into the reaction mixture were suitable for X-ray crystal structure analysis.

The copper(II) nitrate and cadmium nitrate complexes, **3.78** and **3.79**, were prepared by the reactions of **3.71** with $Cu(NO_3)_2$ and $Cd(NO_3)_2$ in methanol, respectively. The complexes were isolated as blue and white complexes in high yields, 90% and 97%, respectively. The complexes analysed as [M.(**3.71**).$n$$H_2O$], with n=1½ for the copper complex and n=1 for the cadmium complex. The cadmium complex was soluble in DMSO, however, an NMR analysis showed only noncoordinated ligand. The copper complex was insoluble in common solvents. The 1:1 stoichiometry found might suggest some sort of polymeric structure. No further analysis was undertaken in either case.

The zinc bromide complex, **3.80**, was isolated from the reaction of $ZnBr_2$ with **3.71** in methanol as a white powder. The complex analysed with the interesting 3:2 metal-ligand stoichiometry, similar to the silver tetrafluoroborate complex **3.77**. The complex was insoluble in common solvents, and despite numerous attempts, no X-ray quality single crystals could be formed. The insolubility might possibly indicate a polymeric structure. No further analysis was undertaken.

Crystal structure of **3.77**

The silver tetrafluoroborate structure, **3.77**, crystallizes in the triclinic space group P-1. The asymmetric unit contains one molecule of **3.71**, one and a half silver tetrafluoroborates and two acetonitrile solvate molecules. This stoichiometry corresponds to the M_3L_2 stoichiometry found in the elemental analysis. The complex has a one-dimensional polymeric structure, with the polymer made up of 28-membered macrocyclic units linked by silver atoms, as shown in figure 3.68.

The 28-membered macrocycles surround centres of inversion, which relate the two halves. The silver atoms of the macrocycle are coordinated by two pyridine nitrogen atoms, with Ag-N bond lengths of 2.146(2)Å and 2.152(2)Å and have a slightly distorted linear coordination geometry [N-Ag-N 174.27(9)°]. The silver atoms which link the macrocyclic units to form the polymeric chain reside on centres of inversion, with an Ag-N bond length of 2.183(2)Å and a strictly linear coordination geometry.

The ligand molecules are remarkably planar, with the pyridine rings of the macrocycle tilted by 7.1(2)° and 5.7(2)° to the benzene ring, and the linking pyridine tilted at an angle of 11.1(2)° to the benzene ring. The macrocycle is also quite planar, with a mean deviation of only 0.112(5)Å from planarity for its 28 atoms. The planarity of the polymer allows the adjacent chains to be involved in π-π face-to-face interactions. The closest of these

interactions occurs between one of the pyridine rings and a benzene ring of an adjacent chain. These rings are almost coplanar [7.1(2)°] and slightly offset, with C2A 3.34(4)Å above the centre of the benzene ring.

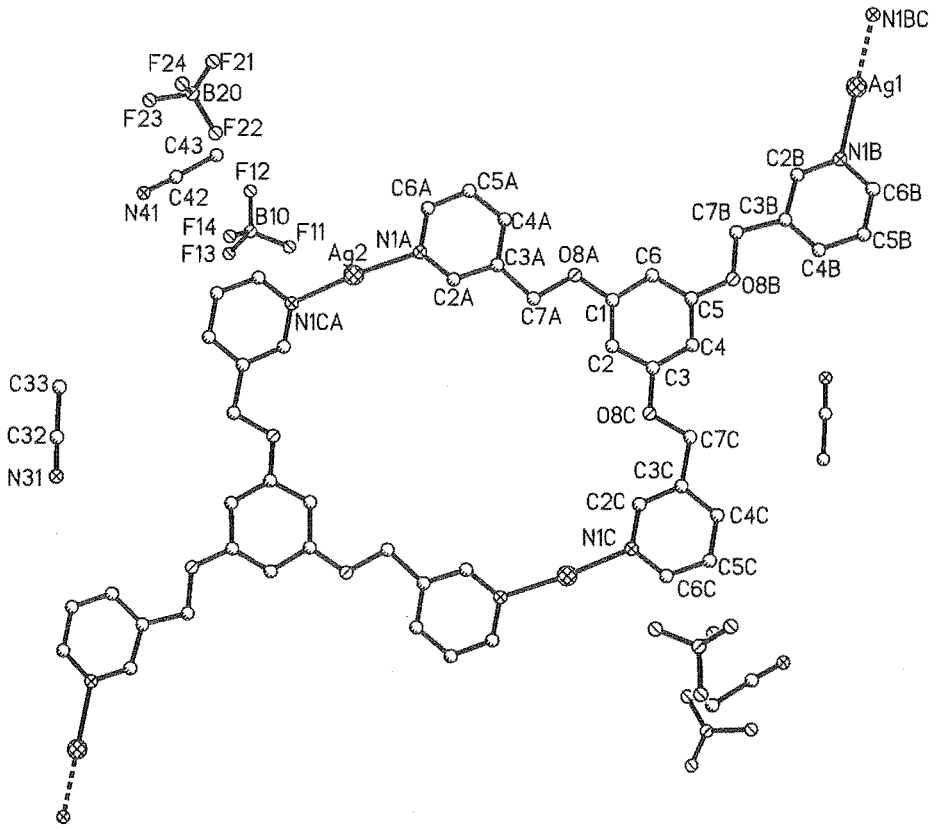
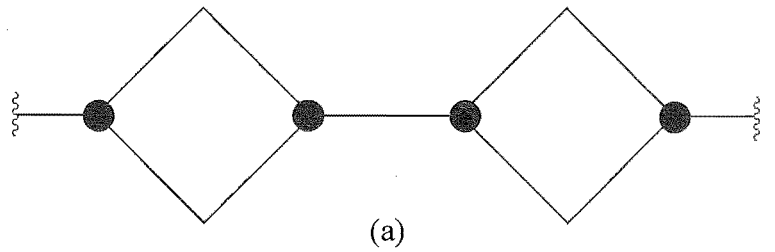


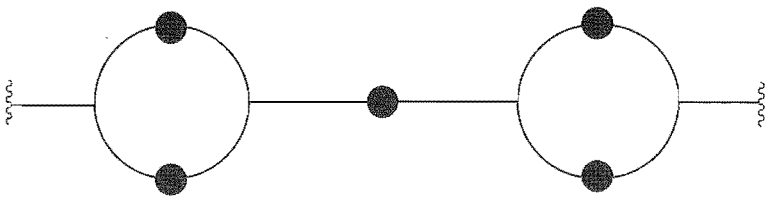
Figure 3.68 Perspective view of a section of polymeric chain of the structure of **3.77**, with atomic labelling shown. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N1B 2.183(2), Ag2-N1A 2.146(2), Ag2-N1CA 2.152(2), N1A-Ag2-N1CA 174.27(9).

The planarity and proximity of the chains also allows an Ag···π interaction to occur between Ag1 and the C2-C3 bond of an adjacent benzene ring. This interaction is not symmetrical, with distances of 3.339(3)Å and 3.378(3)Å between the silver atom and C2 and C3, respectively. The interaction is quite weak compared with other silver-arene complexes, which typically have bonding distances of about 2.6Å.[149] The distance from the silver atom to the midpoint of the double bond is 3.286(4)Å, which is shorter than the proposed silver-double bond to van der Waals interaction distance of 3.42Å.[150]

The one-dimensional polymeric chain of 'loops' topology of **3.77**, while rare, has been described on various occasions.[17] These polymers usually involve flexible bidentate ligands and metals atoms which bridge three ligand molecules. This topology is represented in figure 3.69(a). The cadmium nitrate complex of 1,2-bis(4-pyridyl)ethane forms a simple example with this type of topology.[78] The zinc nitrate and silver nitrate complexes of 1,4-bis(1-imidazolylmethyl)benzene have similar structures, which are slightly more complex due to interpenetration of the polymeric strands to form a two-dimensional polyrotaxane network[151] and a polyrotaxane column,[152] respectively. There are also examples of structures with this topology utilising more rigid ligands such as the silver hexafluorophosphate complex of 1,4-bis(3-pyridyl)1,2,4,5-tetrazine.[153] The structure of **3.77** has a similar topology, as shown in figure 3.70. However, the structure of **3.77** represents the first example of this topology type where the roles of the components have been reversed, as represented in figure 3.69(b). In this case the flexible ligand is tridentate and the silver atoms each bridge two ligand molecules, giving an M_3L_2, rather than an M_2L_3, stoichiometry for the polymer.



(a)



(b)

Figure 3.69 Cartoon representation of possible one-dimensional polymeric 'loop' topologies. **(a)** Three coordinate metal and bidentate ligand, **(b)** two coordinate metal and tridentate ligand.

The polymers of **3.77** arrange with coplanar chains stacked offset by half a ligand unit. This offset gives the structure a 'honeycomb' appearance, with columnar channels, as shown in figure 3.71. These channels contain the tetrafluoroborate counterions and

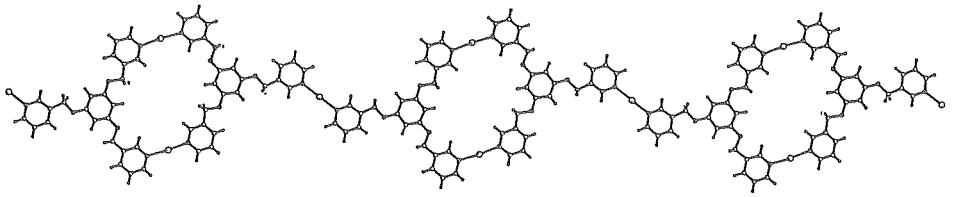


Figure 3.70 View of the one-dimensional polymeric 'loop' topology of **3.77**. The tetrafluoroborate counterions and acetonitrile solvate molecules have been omitted for clarity.

acetonitrile solvate molecules. One of the tetrafluoroborate counterions resides on a centre of inversion, and is therefore disordered over two orientations. Both of the tetrafluoroborate counterions are involved in numerous CH···F interactions with H···F distances between 2.30Å and 3.00Å. The majority of their interactions occur between the tetrafluoroborate counterions and the acetonitrile solvate molecules, which in turn weakly interact with the silver atoms of the polymeric chains, with Ag···N distances in the range 2.78 – 2.96Å.

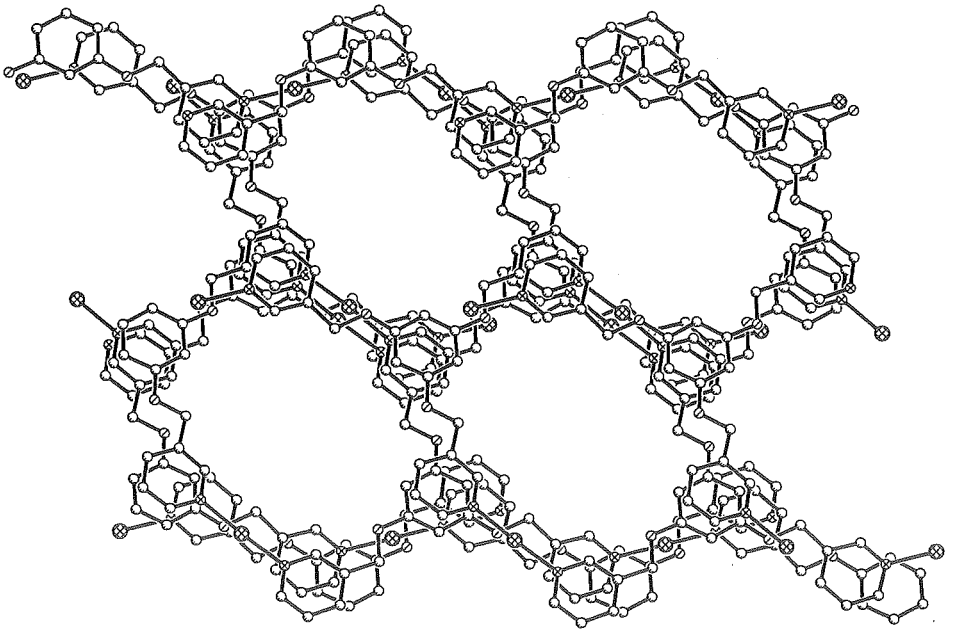


Figure 3.71 View of the honeycomb appearance of **3.77**, showing the channels which hold the tetrafluoroborate counterions and acetonitrile solvate molecules. The hydrogen atoms, tetrafluoroborate counterions and acetonitrile solvate molecules have been omitted for clarity.

3.7.4 Coordination chemistry of 3.72

The coordination chemistry of **3.72** was investigated by formation of complexes with $AgBF_4$ (**3.81**), $Cu(NO_3)_2$ (**3.82**), $Cd(NO_3)_2$ (**3.83**) and $ZnBr_2$ (**3.84**). The silver tetrafluoroborate complex, **3.81**, was isolated as a fawn precipitate from the reaction of **3.72** with $AgBF_4$ in acetonitrile. The complex analysed as $[AgBF_4.(\mathbf{3.72}).H_2O]$. Despite numerous attempts, no crystals suitable for X-ray structure analysis were grown and no further characterisation was undertaken.

The copper(II) nitrate and zinc bromide complexes, **3.82** and **3.84**, were prepared by the reactions of **3.72** with $Cu(NO_3)_2$ and $ZnBr_2$ in methanol, respectively. The complexes both analysed with a 1:1 metal-ligand stoichiometry and were insoluble in common solvents. The insolubility and stoichiometry might possibly indicate a polymeric structure for the complexes. No further analysis was undertaken.

The cadmium nitrate complex, **3.83**, was prepared by the reaction of **3.72** with cadmium nitrate in 1:1 dichloromethane-methanol solution. The complex formed as large rod-like crystals in 68% yield, which analysed with a 1:1 metal-ligand stoichiometry. The crystals isolated from the reaction mixture were suitable for X-ray structure analysis.

Crystal structure of **3.83**

The cadmium nitrate complex, **3.83**, formed as large colourless rod-like crystals which lost solvent extremely quickly to form a colourless powder. After numerous attempts, a crystal was transferred to the cold nitrogen stream of the diffractometer before the crystallinity was lost. However, the crystal diffracted only weakly and the data collected could only be refined to R_1=11%. The complex crystallizes in the face centred monoclinic space group C2/c, with one molecule of **3.83**, one cadmium nitrate and disordered methanol, dichloromethane and water solvate molecules in the asymmetric unit. The complex has a three-dimensional polymeric network structure. The ligands each bridge three cadmium atoms, as shown in figure 3.72.

The heptacoordinate cadmium atom is chelated by two nitrate anions, with Cd-O bond lengths in the range 2.37(1) – 2.459(8)Å. The cadmium is also coordinated by the pyridine nitrogen atoms of three molecules of **3.72**. The cadmium atom forms a 'T-shaped' connector between the ligand molecules, with two near right angles [N-Cd-N angles of 93.1(3)° and 94.8(3)°] and one almost linear [169.0(4)°]. The Cd-N bond lengths of

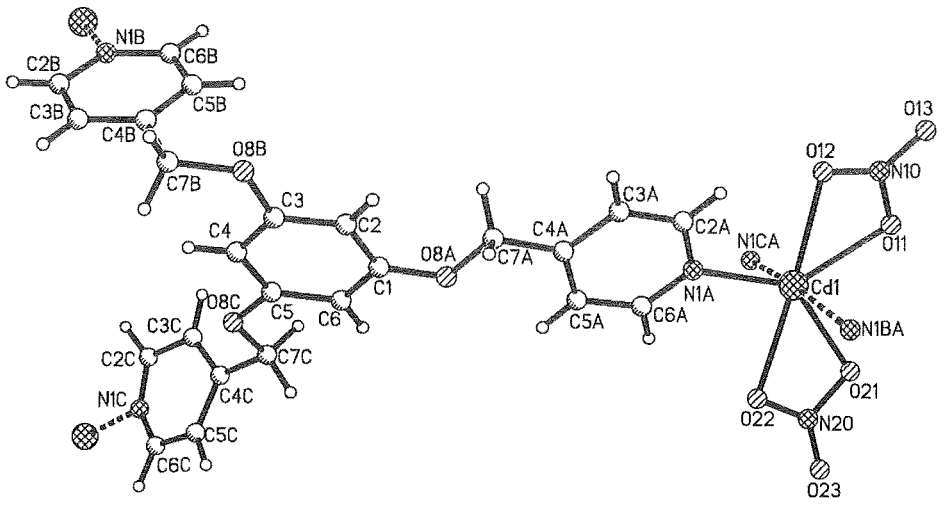


Figure 3.72 Perspective view of a section of the three dimensional polymeric structure of **3.83**. The disordered methanol, dichloromethane and water solvate molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cd1-N1CA 2.30(1), Cd1-N1BA 2.307(7), Cd1-N1A 2.299(9), Cd1-O11 2.373(9), Cd1-O21 2.37(1), Cd1-O12 2.43(1), Cd1-O22 2.459(8), N1CA-Cd1-N1BA 169.0(4), N1CA-Cd1-N1A 93.1(3), N1BA-Cd1-N1A 94.8(3).

2.30(1)Å, 2.307(7)Å and 2.299(9)Å are within range of other Cd-N bond lengths found in this work. Heptacoordinate cadmium nitrate complexes involving two chelating nitrate anions have been found to form 'T-shaped' connectors, and, in combination with linear bridging ligands, give numerous structural motifs.[109,129,132,154]

The combination of the 'T-shaped' cadmium atoms and the tridentate ligands gives the complex an elaborate three-dimensional structure. The pyridine rings of the ligand are tilted at angles of 70(2)°, 77(2)° and 15(2)° to the benzene ring. The three-dimensional network contains large M_5L_5 macrocycles. The polymeric network structure forms with large cavities parallel to the *b*-axis, as shown in figure 3.73. These columns contain the disordered solvate molecules, which could not adequately be identified due to the poor refinement.

The complexes formed from the flexible molecules **3.70** – **3.72** reflect the variety of structures that these ligands can form. The silver nitrate and zinc bromide complexes of **3.70** have discrete macrocyclic structures. These have similar topologies despite the coordination of only two metals in the zinc bromide case, compared with four in the silver

nitrate structure. The formation of discrete macrocycles was observed by both Hartshorn and O'Keefe during their studies of ligands formed from 2-pyridyl heterocycles.

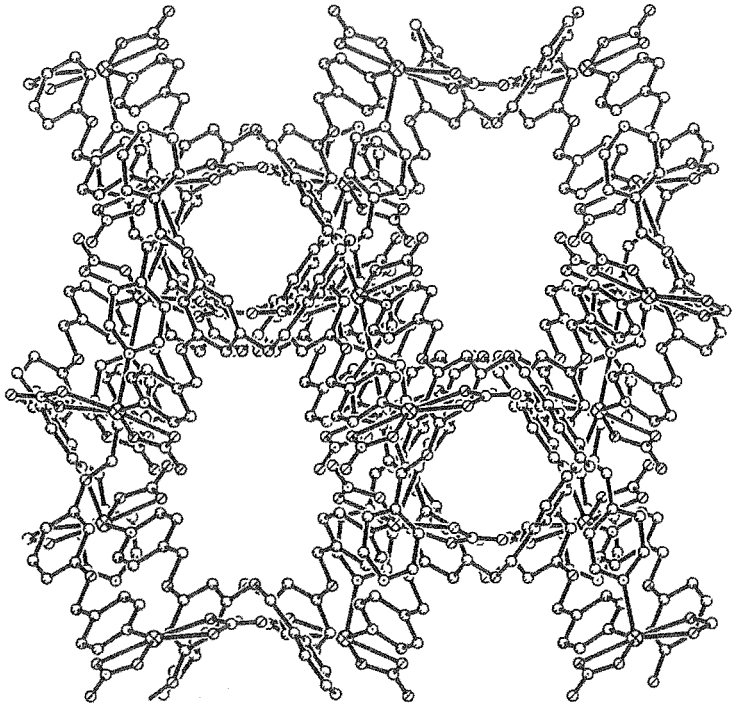


Figure 3.73 View of the solvent containing columns of **3.83**.

The formation of polymeric complexes from ligands **3.70** – **3.72** shows these ligands can be used as three-way connectors for the formation of coordination polymers and networks. Traditional approaches to such polymeric topologies use ligands with only two donor sites combined with metals with varied numbers of possible coordination sites to generate structural complexity. The flexibility of **3.70** – **3.72** allows the formation of topologies such as the [6,3]-net and a one-dimensional polymer of 'loops' with the common structural roles reversed; both the metals in these structures coordinate only two ligands.

3.8 Conclusion

The investigation of the metallosupramolecular chemistry of the fifteen novel flexible ligands prepared above has shown that a wide range of structures are possible with a variety of metal atoms. It was hoped at the outset that the introduction of small flexible linkers between the heterocyclic rings and the aromatic ring would allow the formation of

complexes with ligands in various conformations, which would be unavailable to more rigid linear and angular ligands.

The multinodal ligands **3.1** and **3.2** gave interesting two-dimensional structures with copper(I) iodide. The increase in the length of the spacer groups to two units (-CH_2O-) allowed the formation of a more diverse range of structures. The majority of the complexes analysed by single crystal X-ray structure analysis had one-dimensional polymeric structures. In order to form two-dimensional nets, extra interactions were necessary. In one case these were supplied by a weak Ag···Ag interaction. Increasing the number of nitrogen donor atoms from two to three also allowed the formation of a two dimensional net. Three connector ligands and two connector metals gave an interesting one-dimensional polymer. Discrete structures formed more rarely as is to be expected for the ligands used, which were mostly *exo*-bridging.

Interestingly, in many of the complexes weaker interactions were observed, and these could play a role in the topologies observed. The aromatic parts of the ligands, the core and heterocycles, were usually involved in π-π interactions, with both face-to-face and edge-to-face interactions observed. Hydrogen bonding interactions were also observed, however, these mostly relied on water molecules and oxygen containing counterions, as the ligands only contained hydrogen atoms bound to carbons atoms.

The flexibility of the ligands used in this chapter resides in the linker group used to append the heterocycles to the benzene core (fig 3.3). In the crystal structures of coordination complexes this flexibility was manifested in two ways, (a) the conformation of the flexible linker, and (b) the angle of the meanplane of the heterocycle to that of the benzene ring. The conformation of the flexible linker was observed to be either *anti* or *gauche*, with the former the more energetically stable. The change in conformation of this bond should allow for many different structures to be formed from flexible ligands. However, of the 24 crystal structures involving ligands capable of these conformations, in only two cases was it observed. The tilting of the heterocycles relative to the benzene ring was observed on more occasions, with angular arrangements observed in just under 75% of the structures. The formation of helical polymers and 'necklace' polymers was associated with ligands comprising one or two tilted arms.

These results suggest when employing flexible ligands it is more likely to observe all-*anti* backbones, and any *gauche* arrangements will be the exception. The separation of the heterocyclic rings from the aromatic rings by intermediate length flexible chains allows these rings to tilt, which leads to the formation of interesting topologies. The preparation of

ligands containing more than two donor atoms in an *exo*-type arrangement allows the formation of a larger range of topologies with ligands bridging more than two metal atoms.

Chapter 4

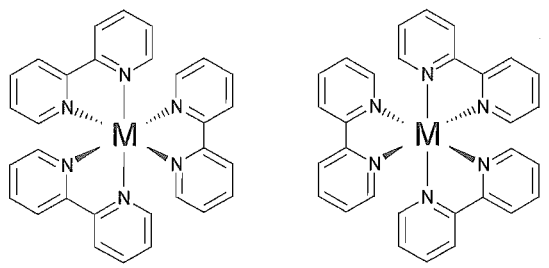
Chiral Coordination Polymers

4 Chiral Coordination Polymers

4.1 Introduction

The chemistry of chiral compounds, both organic and inorganic, is of great importance to the study of many areas in chemistry, biology and physics.[64,155] The use of chiral coordination compounds is particularly prevalent in asymmetric catalysis.[156] The chirality of tetrahedral centres based on carbon atoms has become a well developed area since its inception by van't Hoff in the latter half of the 19th century.[157] In contrast, the chiral chemistry of inorganic compounds was long ignored after the pioneering investigations into the stereochemistry of transition metal complexes by Werner and co-workers.[158] The last 30 years have seen a rapid resurgence in the study of chiral coordination compounds, largely driven by improvements in techniques of structure determination, such as NMR spectroscopy and X-ray crystal structural analysis.[155]

The stereochemistry of coordination compounds is typically discussed in terms of square planar and octahedral geometries. The latter of these, for coordination of three chelating bidentate ligands, give rise to Λ and Δ isomers, as shown in figure 4.1. These disymmetric structures form an enantiomeric pair, and are the basis for the majority of investigations of chiral coordination compounds. Square planar complexes can also have metal-centred chirality, if the geometry is distorted from planarity. This leads to helical complexes, which can be designated as Δ or Λ depending on the handedness of the helix.[155] As square planar chirality relies on a distortion from normal square planar geometry it is not as common as that of octahedral complexes. Chirality at metal centres with geometries other than octahedral or square planar is possible.[155] However, the majority of such complexes are quite labile, and this makes isolation and characterisation problematic.



Λ Δ

Figure 4.1

The formation and isolation of chiral coordination compounds based on octahedral metal centres has recently been the focus of intensive study. However, the resolution of mixtures of chiral compounds can prove problematic. In some cases one of the components of the racemate or mixture may preferentially crystallize with a chiral counterion,[64] such as 10-camphorsulfonate.[159] The separation of mixtures of chiral mononuclear and oligonuclear complexes of ruthenium and osmium by chromatographic techniques has been developed by Keene. This involves the use of a cation exchange resin and large anions for the best results.[160]

While achiral starting materials can give racemic mixtures of chiral complexes, it has been observed that chiral starting materials often preferentially give individual stereoisomers. The use of chiral metal complexes as precursors has shown moderate success; however, this approach is limited by the availability of starting materials. Formation of individual stereoisomers from chiral ligands has been more effective. This uses well developed techniques available from organic synthesis, particularly the use of chiral precursors available from the 'chiral pool'.[161]

Complexes of multidentate ligands derived from chiral molecules have been the subject of an excellent recent review.[162] Ligands with attached pinane groups have been studied extensively by the group of von Zelewsky.[163] These ligands consist of a pinane skeleton fused to a substituted pyridine ring, for example those molecules shown in figure 4.2. These so-called 'chiragen' molecules have been used in the formation of numerous chiral complexes, which usually contain one stereoisomer. Various different topologies have been observed, with the formation of square planar and octahedral mononuclear complexes[164] and both circular[165] and linear helicates.[166]

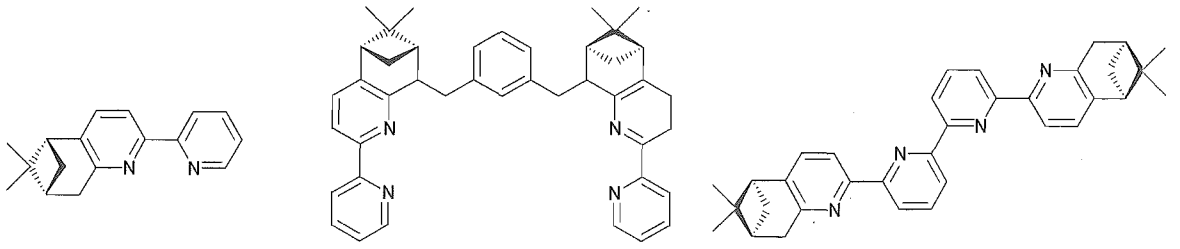
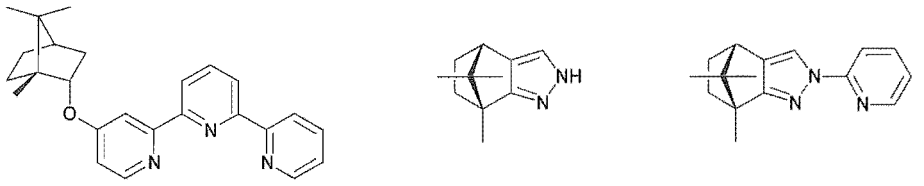


Figure 4.2

The use of other chiral natural products, such as camphor, has been investigated. Camphor and some of its simple derivatives are readily available from commercial sources as single stereoisomers. The attachment of a borneol moiety to pyridine based N-

heterocyclic molecules is a simple method for the production of chiral ligands, with the preparation of different enantiomers relying on the chirality of the starting material. The borneol substituted terpyridine molecule shown in figure 4.3(a) was used by Constable et al. to form helicates with copper(I) and silver.[167] The camphor-fused heterocycle, camphopyrazole (fig 4.3(b)), was used by Hartshorn[107] and Watson.[168] They produced numerous ligands based on this molecule, such as the chelating ligand shown in figure 4.3(c), which forms mononuclear complexes with various metal atoms.[169]



(a) (b) (c)

Figure 4.3

The chiral ligands described thus far have been used to form mainly discrete mononuclear and oligonuclear complexes. The formation of chiral coordination polymer structures containing one stereoisomer is less well studied. Linking octahedral metal centres of predetermined chirality to form a chiral polymer can be achieved using other more labile metal atoms,[170] or through reaction of the coordinated ligands.[171] The serendipitous or predetermined formation of helical polymers, which are chiral, is possible (see chapter 3). However, the formation of helical polymers containing only one enantiomer is not assured when using achiral starting materials, and such examples are rare.[134,172] The arrangement of strands in a network can confer chirality on the overall structure,[173] and this has been observed in the formation of chiral networks from achiral starting materials.[44,174] Complexes bridged by chiral anions, such as amino acid derivatives[175] and lactate,[176] have been used to form chiral coordination polymers. Ligands with attached chiral groups have found limited use for the formation of polymers. The bridging pinane based ligand shown in figure 4.4 was used to form a helical polymer with iron, which was isolated as a single enantiomer.[177]

This chapter investigates the synthesis of simple ligands with one or more camphor groups fused to an *exo*-bridging heterocycle (outwardly oriented donor atoms). The coordination chemistry of any potential ligands prepared are then examined to determine if these potential ligands can give rise to chiral coordination polymers. The use of labile

metal atoms means that the complicating factor of metal stereochemistry will be avoided, with the chirality of any complex formed conferred by the asymmetry of the ligands.

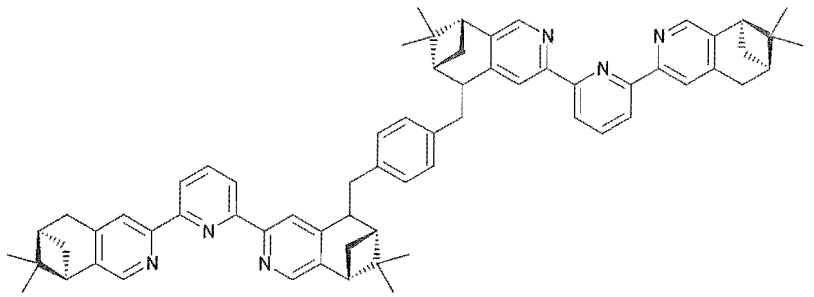
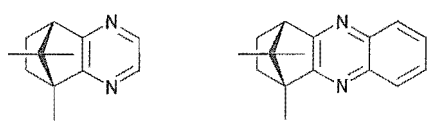


Figure 4.4

4.2 Ligands with one fused camphor

Pyrazine has been used extensively as a linear *exo*-bridging ligand, and is second only to 4,4′-bipyridine for this purpose.[33] The majority of these complexes have discrete dinuclear structures. Such complexes are used to investigate mixed valence compounds, such as the Creutz-Taube ion.[178] Pyrazine has also been used in the formation of discrete macrocyclic complexes, giving triangles,[179] squares[35,180] and rectangles[181] under appropriate conditions. Polymeric complexes involving pyrazine are quite common, with the most abundant metals used being copper(I) and silver. The type of coordination polymer isolated depends on the preferred geometry of the metal atom and the anion used, with one-dimensional polymers and two-dimensional nets the most common topologies observed.[182]

The potential *exo*-bridging ligands camphopyrazine (**4.1**) and camphoquinoxaline (**4.2**), shown in figure 4.5, were synthesised to investigate the formation of chiral coordination polymers. The single camphor group fused to the pyrazine and quinoxaline ring confers chirality to these molecules, which will be preserved during the formation of any complexes.

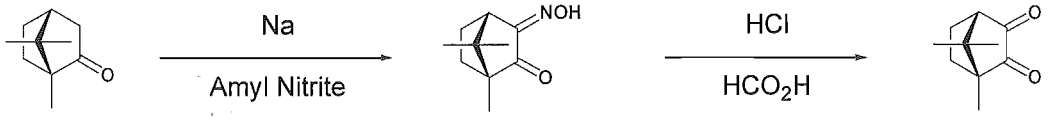


4.1 **4.2**

Figure 4.5

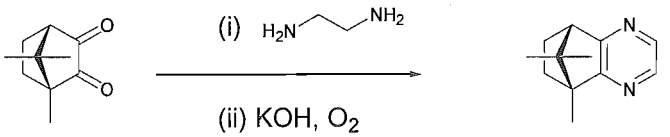
4.2.1 Ligand Synthesis

The potential ligands camphopyrazine (**4.1**) and camphoquinoxaline (**4.2**) were synthesised using the methods of Elguero and Shimizu.[183] The starting material for both the ligands was natural camphor, which contains only one enantiomer ((1R)-(+)-camphor, supplied by BDH). This can be converted to camphorquinone in high yield by reaction with selenium dioxide.[184] Given the toxicity of this reagent, an alternative two step synthesis combining the methods of Foster and Rao, [185] with that of Love and Jones,[186] was developed. The initial step involved the synthesis of camphor-3-oxime, using sodium metal and amyl nitrite, followed by the conversion to camphorquinone using the method of Love and Jones. This involved the reaction of camphor-3-oxime with formic acid in a hydrochloric acid solution, as shown in scheme 4.1.



Scheme 4.1

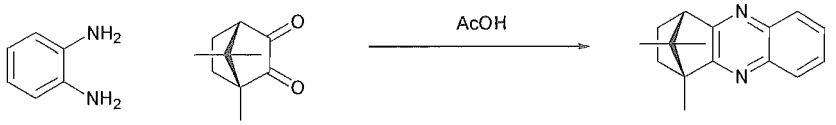
The precursor to camphopyrazine (**4.1**), dihydrocamphopyrazine, was prepared by the reaction of camphorquinone and ethylenediamine in benzene with *p*-toluenesulfonic acid under Dean-Stark conditions. The product formed was oxidised by bubbling oxygen gas through an ethanolic solution containing KOH and dihydrocamphopyrazine, to give **4.1** in 69% overall yield, as shown in scheme 4.2.



4.1

Scheme 4.2

Camphoquinoxaline (**4.2**) was synthesised by the reaction of freshly sublimed *o*-phenylenediamine and camphorquinone in acetic acid, as shown in scheme 4.3. The product was purified by chromatography and recrystallization to give **4.2** in 54% yield.



4.2

Scheme 4.3

4.2.2 Coordination complexes

The coordination chemistry of **4.1** was investigated by preparation of complexes with $AgNO_3$ (**4.3**), $Cu(NO_3)_2$ (**4.4**), CuI (**4.5**) and $ZnBr_2$ (**4.6**). The preparation of complexes with $PdCl_2$ and $Cd(NO_3)_2$ was also attempted. However, all attempts to isolate products from these reactions proved fruitless. The inability to form complexes with these two metals may be due to the sterically crowded nature of the nitrogen donor atoms of **4.1**.

The silver complex, **4.3**, was isolated from the reaction of **4.1** with $AgNO_3$ in a 1:1 mixture of acetone-methanol. The crystalline product obtained analysed as [$AgNO_3$.(**4.1**)]. The crystals isolated from the reaction mixture were too small to permit an X-ray structure analysis. Suitable crystals were obtained from the slow evaporation of an acetonitrile solution of **4.3**.

The copper(II) nitrate complex, **4.4**, was isolated after the almost complete evaporation of a methanol solution of **4.1** and $Cu(NO_3)_2$. The light-blue crystals formed analysed with an intriguing 4:3 metal-ligand stoichiometry. The crystals were extremely thin, and, despite numerous attempts, were the only crystalline material isolated from reactions of **4.1** with $Cu(NO_3)_2$. The thin blue plate-like crystals of **4.4** were used for an X-ray structure determination.

The reaction of **4.1** with CuI in acetonitrile gave a yellow solution. Slow evaporation of this yellow solution produced yellow crystals of a copper(I) iodide complex (**4.5**). The crystals analysed as [CuI.(**4.1**)], and an NMR spectrum of the complex in acetonitrile showed a set of peaks indicating all the molecules of **4.1** in the product are equivalent. The complex was also analysed using electrospray mass spectrometry, which indicated a range of species involving various combinations of copper, **4.1** and acetonitrile. The crystals isolated from the reaction mixture were suitable for X-ray structure analysis.

The zinc dibromide complex, **4.6**, was isolated from the slow evaporation of a methanol solution of **4.1** and $ZnBr_2$. The colourless crystals analysed with a 1:1 metal-ligand stoichiometry. An NMR spectrum of the complex in acetonitrile showed only

uncoordinated ligand. The crystals isolated from the reaction mixture were suitable for X-ray crystal structure analysis.

Despite numerous attempts to from coordination complexes with **4.2**, none could be isolated. Reactions with silver salts gave black or brown reaction products, possibly indicating oxidation. Reactions with other metals gave solutions, which upon evaporation of solvent, gave a white solid which was identified as **4.2**. The inability to form coordination complexes could be due to the sterically hindered nature of the nitrogen donor atoms of **4.2**.

Crystal structure of **4.3**

The silver nitrate complex, **4.3**, crystallizes in the monoclinic space group C2, and has a one-dimensional polymeric structure. The asymmetric unit contains one molecule of **4.1** and one silver nitrate. The silver atoms are bridged by the nitrogen atoms of the ligand, as shown in figure 4.6. The two nitrogen atoms have different steric environments, with one

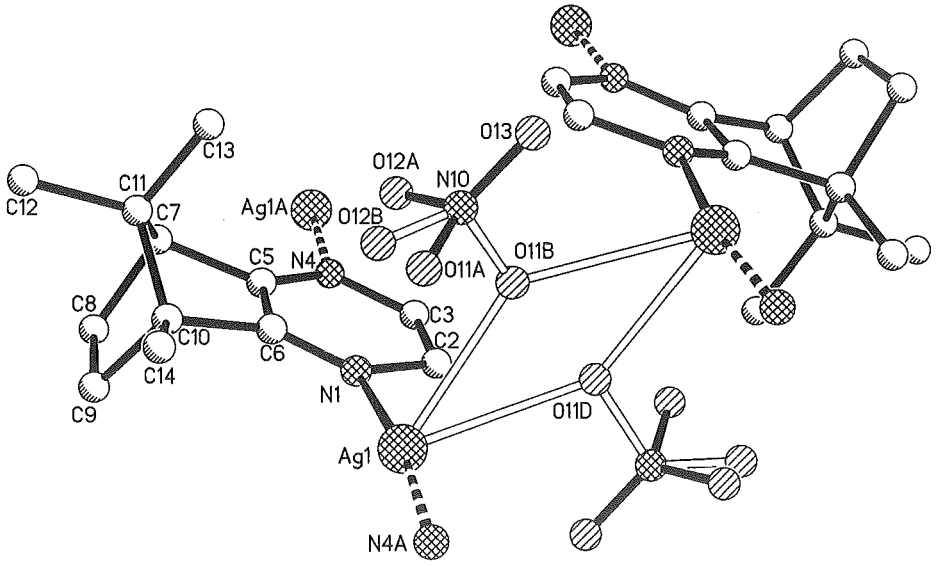


Figure 4.6 Perspective view of the structure of **4.3**, showing the disordered nitrate anions. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N4A 2.18(2), Ag1-N1 2.28(2), Ag1-O11D 2.48(1), Ag1-O11B 2.55(1), N4A-Ag1-N1 173.0(2), N4A-Ag1-O11D 96.4(8), N1-Ag1-O11D 89.1(8), N4A-Ag1-O11B 96.9(8), N1-Ag1-O11B 90.0(8).

(N1) having an adjacent methyl group and the other (N4) an adjacent hydrogen atom. This affects the Ag-N bond distances, with the more sterically hindered nitrogen having a slightly longer bond length of 2.28(2)Å, as opposed to 2.18(2)Å for the less hindered nitrogen atom.

The bridging nitrate anions link adjacent polymer chains giving a 'ladder-like' polymeric structure, as shown in figure 4.7. The chains of the 'ladder' are related by a two-fold rotation axis, which lies between the silver atoms. The chains propagate along the *b*-axis of the unit cell, with the distance between the silver atoms of the chains 4.67(1)Å. The ligands of the 'ladder' polymers arrange in a head-to-tail fashion, with the methyl-groups oriented in the same direction. This is identical for all the polymeric chains, due to the reduced symmetry of the space group C2.

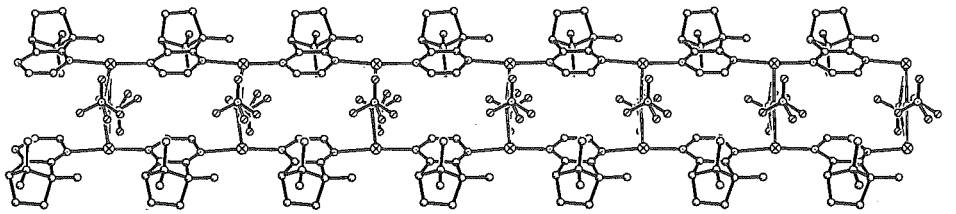
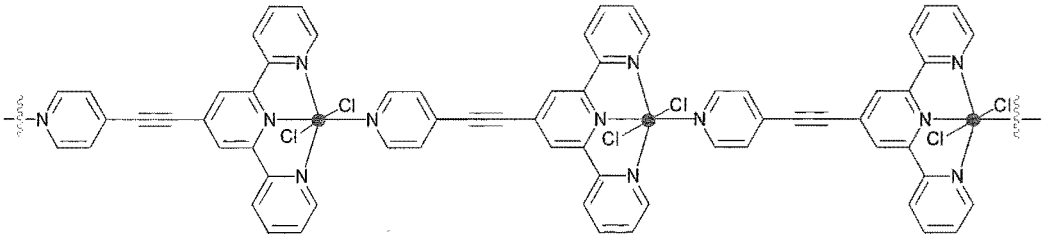


Figure 4.7 Perspective view of a section of the 'ladder' polymeric structure of **4.3**. The hydrogen atoms have been omitted for clarity.

The unsymmetrical nature of the nitrogen donors of **4.1** allows the possibility that the polymers will form with defined directionality. This has been an area of recent interest, with the most common approach being the design of *exo*-ligands with different donor sites at either end.[187] The combination of these ligands with metals that can simultaneously be coordinated by the different ends of the ligand can give polymers that are directional by nature, as shown in figure 4.8.[188]

The unsymmetrical molecule, **4.1**, is an *exo*-ligand with donor sites that differ in their steric environment. The faithful head-to-tail alignment of the ligand molecules gives the chains of **4.3** directionality, and as a consequence of the 2-fold axis, the overall 'ladder' structure has directionality also. The ligands used in the formation of directional polymers thus far have been achiral, and have lead to centrosymmetric structures which contain directional polymers oriented in opposite directions, as represented in figure 4.9(a).

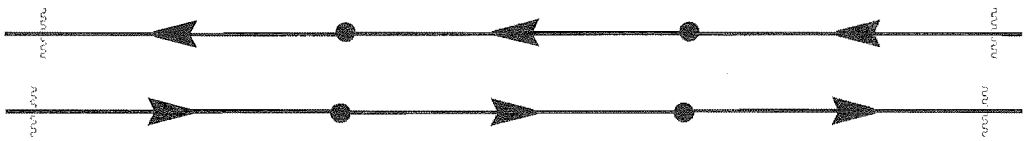


(a)

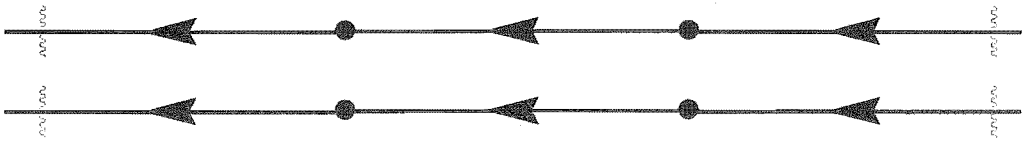
(b)

Figure 4.8 **(a)** An example of a directional polymer consisting of an *exo*-ligand with different donor sites at each end, **(b)** a cartoon representation of a directional polymer.

The chiral nature of the molecule **4.1** means that the structure of **4.3** cannot form in a centrosymmetric space-group, which is borne out by the formation of the **4.3** in the chiral space group C2. The possibility still exists for the chains to form oriented in opposite directions. However, this is not the case, with the 'ladder' chains of **4.3** all oriented in the same direction, as represented in figure 4.9(b).



(a)



(b)

Figure 4.9 Cartoon representation of combinations of directional polymers, showing **(a)** centrosymmetric directional polymers, **(b)** non-centrosymmetric directional polymers.

Crystal structure of **4.4**

The light-blue crystals of the copper(II) nitrate complex, **4.4**, were very thin and diffracted X-rays only weakly. However, despite the poor refinement (R_1= 12%), a description of the structure is still possible. The complex crystallizes in the orthorhombic

space group $C222_1$, with an asymmetric unit containing two molecules of **4.1**, two water molecules and one copper(II) nitrate. The complex has a mononuclear structure, as shown in figure 4.10. This structure has 1:2 metal-ligand stoichiometry, which is different to the elemental analysis found for the bulk sample originally isolated (4:3 metal-ligand stoichiometry). Despite numerous attempts, no material suitable for X-ray crystal structure determination with the same stoichiometry as the analytical sample could be isolated.

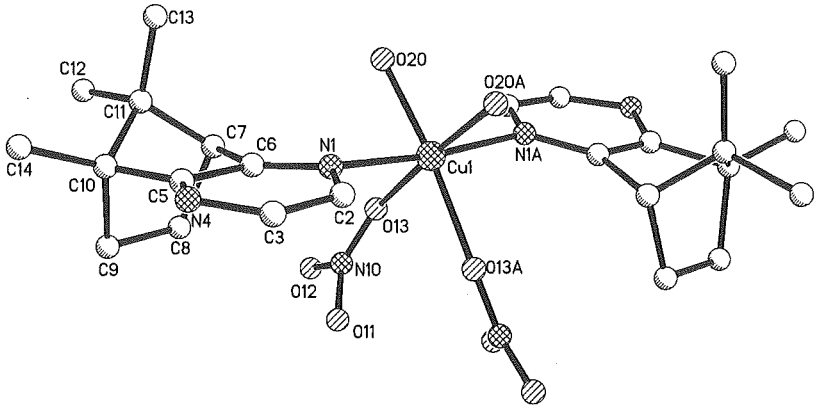


Figure 4.10 Perspective view of the mononuclear structure of **4.4**, showing the major component of the disordered water molecules. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.06(1), Cu1-O13 2.13(1), Cu1-O20 1.94(6), N1A-Cu1-N1 173.5(9), O20-Cu1-N1 84(2), O20-Cu1-O13 90(2), N1-Cu1-O13 94.1(4), O20-Cu1-O20A 92(2), O13-Cu1-O13A 89.6(6).

The copper atom is octahedral, and lies on a two-fold rotation axis parallel to the *a*-axis. The copper is coordinated by four oxygen atoms, consisting of two water molecules and two nitrate anions, and the nitrogen atoms of two molecules of **4.1**. The ligand molecules coordinate through the less hindered nitrogen atom, with a Cu-N bond length of 2.06(1)Å, while the remaining nitrogen atom of the ligand is non-coordinating. The ligand molecules are *trans* across the copper atom, with an N-Cu-N angle that is almost linear [173.5(9)°]. The coordinated oxygen atoms are in a plane, with the nitrate anions being *cis* and having a Cu-O distance of 2.13(1)Å and an O-Cu-O angle of 89.6(6)°. The coordinated water molecules are disordered over two sites, with the major contributing water molecule occupied 60% of the time. The major contributing water molecule has a Cu-O bond length of 1.96(6)Å. The minor contributing water molecule is further away from the copper atom, with a Cu-O distance of 2.48(8)Å.

Crystal structure of 4.5

The copper(I) iodide complex, **4.5**, crystallizes in the monoclinic space group C2, with four molecules of **4.1** and four copper iodides in the asymmetric unit. The complex consists of Cu_4I_4 clusters with each of the copper atoms coordinated by one molecule of **4.1**. The asymmetric unit contains two independent half $Cu_4L_4I_4$ clusters. One of the independent clusters is shown in figure 4.11.

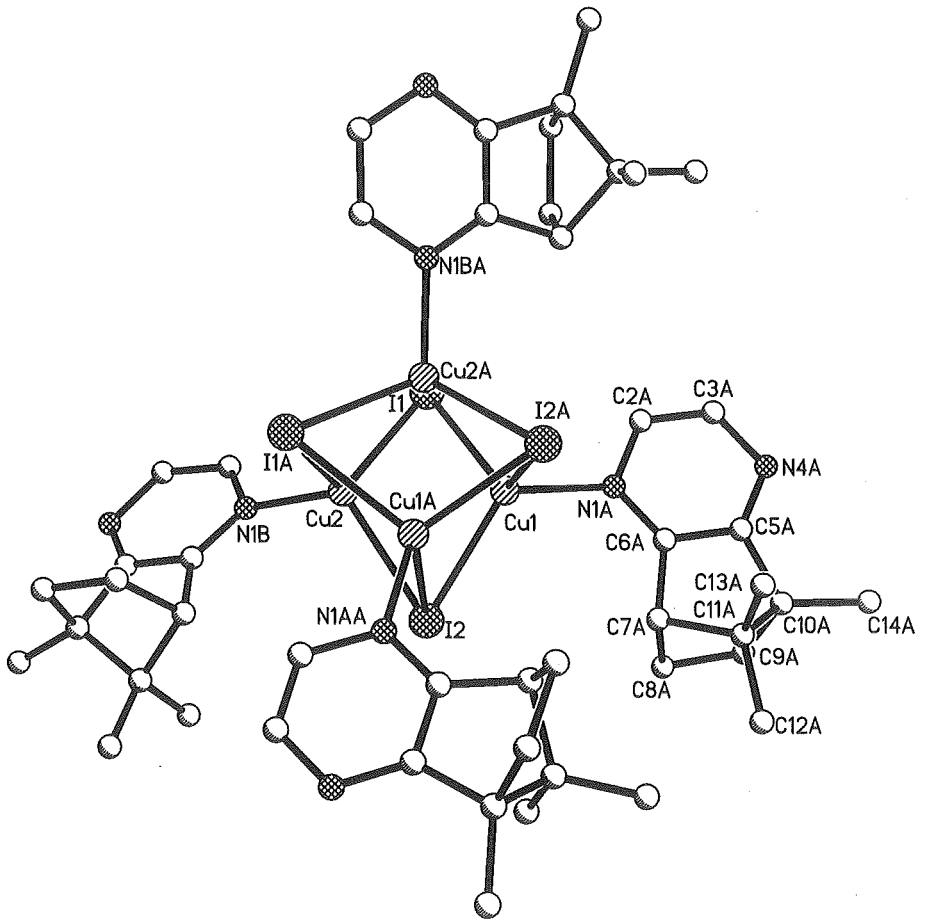


Figure 4.11 Perspective view of the structure of one of the $Cu_4L_4I_4$ units of **4.5**. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N1A 2.043(9), Cu2-N1B 2.030(9), Cu1-I1 2.708(2), Cu1-I2 2.655(2), Cu1A-I2 2.750(2), Cu2-I1 2.673(2), Cu2A-I1 2.718(2), Cu2-I2 2.684(2), N1A-Cu1-I2 119.8(3), N1A-Cu1-I1 105.9(3), I2-Cu1-I1 105.39(5), N1A-Cu1-I2A 95.8(3), I2-Cu1-I2A 113.45(5), I1-Cu1-I2A 116.74(5), N1B-Cu2-I1 108.6(3), N1B-Cu2-I2 110.0(3), I1-Cu2-I2 105.56(5), N1B-Cu2-I1A 101.0(2), I1-Cu2-I1A 112.70(5), I2-Cu2-I1A 118.68(5)

The four copper and four iodine atoms of each cluster form a distorted cube-like structure with the copper atoms forming a tetrahedron. The two independent clusters sit astride a two-fold axis. The Cu_4 tetrahedra of two independent clusters have similar geometries, with Cu···Cu distances in the range 2.670(3) – 2.738(3)Å for one cluster, and 2.648(3) – 2.776(3)Å for the other. The copper atoms all have a tetrahedral coordination geometry, and are each coordinated by three iodine atoms, with Cu-I bond lengths in the range 2.655(2) – 2.769(2)Å. The remaining site of the tetrahedral copper is occupied by the less hindered nitrogen atom of **4.1**, with Cu-N distances between 2.030(9)Å and 2.043(9)Å. The more hindered nitrogen atoms of the molecules of **4.1** remain noncoordinating.

The distorted cube-like cluster is the most common structure found for tetranuclear copper(I) halide complexes, and is more common for iodide complexes than for those of other halides.[189] The cube-like Cu_4L_4 cluster has possible S_4 point symmetry, and the formation of the clusters occupying crystallographic S_4 sites has been observed for a number of complexes utilising nitrogen-donor ligands.[112,190] The coordination of the copper atoms by the chiral ligand, **4.1**, prevents any possible S_4 symmetry, and, in the case of **4.5**, the complex crystallizes in the space group C2, which contains no sites with S_4 cystallographic symmetry. The unit cell of the complex contains two independent copper clusters, which are not related by symmetry. The clusters differ principally in the relative orientation of the molecules of **4.1** that are coordinated to the copper atoms. Similar differences have been observed in the copper(I) iodide complex of pyridine, which crystallizes in the orthorhombic space group $P2_12_12_1$ with one cluster in the asymmetric unit.[191]

Crystal structure of **4.6**

The zinc dibromide complex, **4.6**, crystallizes in the chiral monoclinic space group $P2_1$, with four molecules of **4.1** and two zinc dibromides in the asymmetric unit. The complex consists of two independent zinc atoms, each coordinated by two ligand molecules and two bromine atoms, one of which is shown in figure 4.12.

The zinc atoms are coordinated by two molecules of **4.1**, through the least hindered nitrogen atoms, with Zn-N bond lengths of 2.080(6)Å and 2.086(7)Å for one Zn atom, and 2.089(7)Å and 2.105(6)Å for the other. The zinc atoms are also coordinated by two bromine atoms, with Zn-Br bond lengths in the range 2.3439(2) – 2.3585(2)Å. The zinc

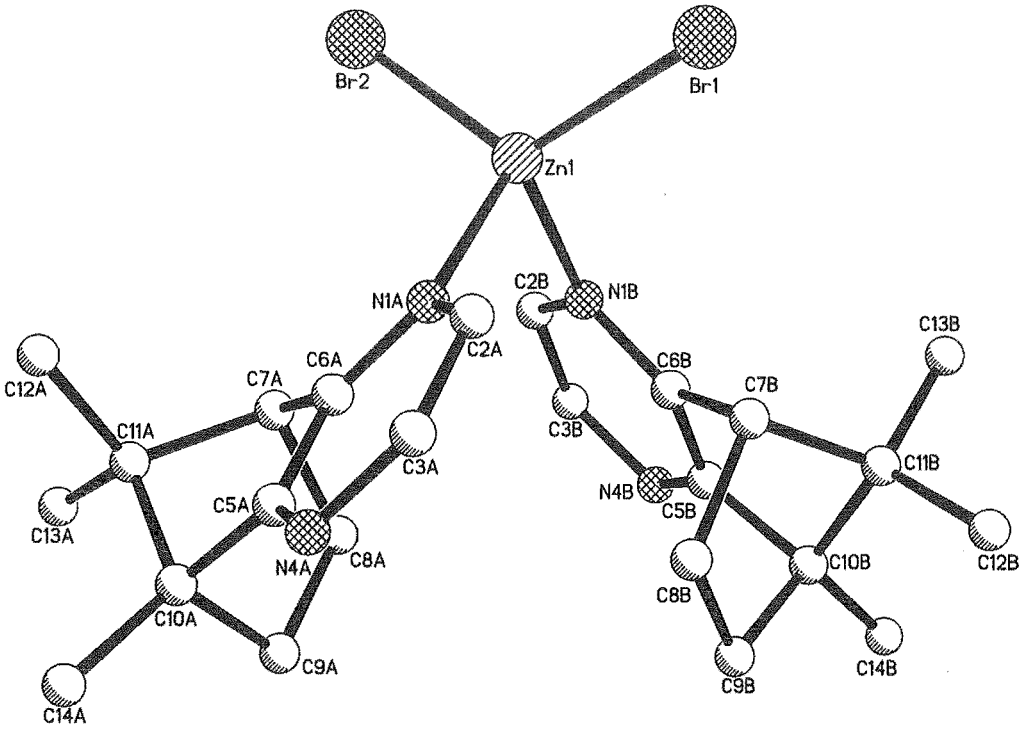


Figure 4.12 Perspective view of one of the zinc complexes of the asymmetric unit of **4.6**, with atomic numbering shown. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn1-N1B 2.080(6), Zn1-N1A 2.086(7), Zn1-Br2 2.3439(2), Zn1-Br1 2.3585(2), N1B-Zn1-N1A 94.4(2), N1B-Zn1-Br2 108.4(2), N1A-Zn1-Br2 111.0(2), N1B-Zn1-Br1 111.3(2), N1A-Zn1-Br1 109.4(2), Br2-Zn1-Br1 119.54(6).

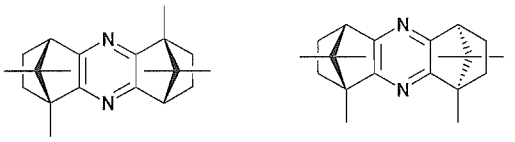
atoms both have slightly distorted tetrahedral coordination environments, with the largest distortion being the angles between the bromine atoms, which are 119.54(6)° and 118.20(6)° for Zn1 and Zn2, respectively. The bond lengths and bond angles of this complex are similar to those found in the tetrahedral zinc dibromide complex of the less sterically hindered molecule pyrazine.[192] However, this complex is a one-dimensional polymer, which in the case of **4.6** is not formed, possibly due to the more sterically hindered coordination environment of the non-coordinating nitrogen atom. There are no significant interactions between the mononuclear units.

The complexes formed from the chiral *exo*-bridging ligand **4.1** show the variety of possible structures available to this ligand. However, only one of these complexes had the desired chiral coordination polymer structure. This could be due to the regioselectivity of complex formation, with the discrete complexes involving coordination to only the less

hindered nitrogen atom of **4.1**. The formation of the silver complex with the directionality of the complex preserved appears to be an effect of this regioselectivity, with the two sites differing only in the steric environment of the nitrogen atoms.

4.3 Pyrazine based ligands with two fused camphors

The complexes formed by the ligand **4.1** above led us to believe that the formation of chiral coordination polymers might be aided by the preparation of potential ligands which differed less significantly in the steric environment of the donor sites. Thus, the ligands *anti*-dicamphopyrazine (**4.7**) and *syn*-dicamphopyrazine (**4.8**) were prepared. The *syn*- and *anti*- prefix in these two cases refers to the relative side of the ring system that the bridgehead methyl groups appear. The nitrogen atoms of **4.7** have identical steric environments, while those of **4.8** differ. The potential ligand **4.7**, therefore, cannot form coordination polymers with any directionality. In contrast the difference in the nitrogen atoms of **4.8** means that this ligand may possibly form directional polymers. It was decided to form complexes with only copper(I) and silver, as these labile metal atoms have been shown to react successfully with sterically hindered nitrogen atoms to form coordination polymers.[22]



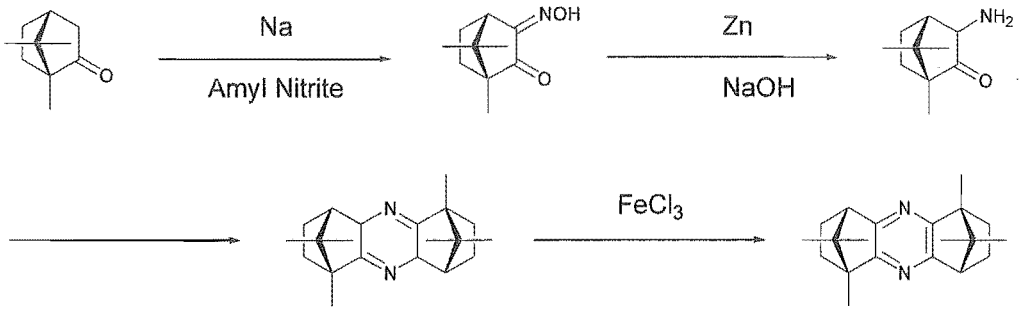
4.7 **4.8**

Figure 4.13

4.3.1 Ligand synthesis

The potential ligand *anti*-dicamphopyrazine (**4.7**) was synthesised from natural camphor using a similar method to that of Forster and Spinner,[193] as shown in scheme 4.4. The synthesis requires camphor-3-oxime, which was available from the synthesis of camphorquinone. This was reduced to 3-aminocamphor using zinc dust in an aqueous NaOH solution. On standing 3-aminocamphor undergoes a spontaneous double condensation reaction to give dihydro-*anti*-dicamphopyrazine. Previously, this has been

oxidised using sodium nitrite in sulfuric acid to give 4.7.[194] The oxidation was carried out using anhydrous ferric chloride, to give 4.7 in 68% yield as a white solid.



4.7

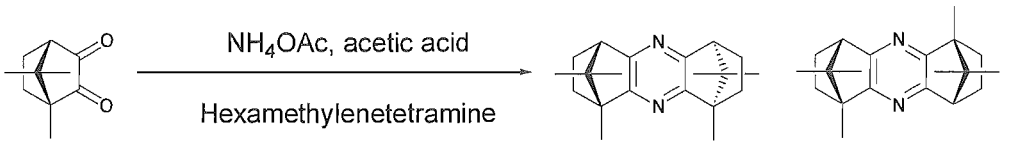
Scheme 4.4

syn-Dicamphopyrazine (**4.8**) has also been synthesised previously. This involved the reaction of 3-aminocamphor with its hydrochloride salt in a sealed tube at elevated temperatures (>220°). The resulting mixture was found to contain both the *syn*- and *anti*-isomers of dicamphopyrazine along with camphor, borneol and unreacted 3-aminocamphor.[195] *syn*-Dicamphopyrazine was isolated from this reaction in low yield (9%), and therefore, a new synthesis needed to be devised.

The synthesis of substituted pyrazine derivatives can be achieved via the reaction of α-keto alcohols with ammonia or ammonium acetate.[196] The α-keto alcohol can be produced *in situ* from a 1,2-diketone using a mild reducing agent such as sodium borohydride.[197] However, the reaction of camphorquinone with ammonium acetate and sodium borohydride in methanol produced none of the desired product, giving only unidentified material and a small amount of camphorquinone starting material. This could be due to the reactivity of the strained camphor skeleton, or the formation of side products.

The Leuckart reaction involves the reductive alkylation of ammonia or ammonium compounds with aldehydes and ketones in the presence of formaldehyde or formic acid.[198] In the presence of acid the reaction has been used to convert aldehydes and ketones into amines. A variation of the reaction has been used to form 1,4-diazines from *o*-quinone compounds. This probably involves the formation of an α-aminoketone that can undergo a double condensation reaction followed by oxidation to form the diazine.[199] The reaction of camphorquinone with ammonium acetate and hexamethylenetetramine in acetic acid gave a 9:1 mixture of **4.8** and **4.7**. Hexamethylenetetramine[200] has been used as a synthetic equivalent for formaldehyde during formation of 4,5-disubstituted imidazoles

from disubstitued *o*-quinones.[201] The mixture of **4.7** and **4.8** was separated by chromatography followed by recrystallization to give **4.8** in 22% isolated yield. This is similar to the stepwise preparation of **4.7**, but represents a one-pot synthesis of a mixture of **4.7** and **4.8** from camphorquinone, rather than the selective formation of one isomer only.



4.8 **4.7**

Scheme 4.5

The isomeric compounds *syn*-dicamphopyrazine (**4.8**) and *anti*-dicamphopyrazine (**4.7**) are indistinguishable by most methods. They differ only in the orientation of the two-fold axis that relates the fused camphor skeletons on either side of the pyrazine ring. The nature of the synthesis of **4.7** from 3-aminocamphor necessitates that only this isomer is formed during the reaction. However, the formation of **4.8** involves a mixture of both isomers, which are then purified by chromatography and recrystallization to separate the isomers. In order to confirm the structural assignments of **4.8** and **4.7** by Rupe and di Vignano,[202] X-ray structure determinations of crystals of **4.7** and **4.8** were undertaken. Crystals of **4.7** and **4.8** were obtained from the slow evaporation of ethanol solutions containing **4.7** and **4.8**, respectively.

The *anti*-isomer, **4.7**, crystallizes in the orthorhombic space group $P2_12_12$, with one half a molecule of **4.7** in the asymmetric unit. The structure of the molecule is shown in figure 4.14. The absolute stereochemistry of the molecule can be correctly assigned by taking into account the starting material for the reaction (natural camphor or (1R)-(+)-camphor (supplied by BDH)). The structure crystallizes with the two-fold axis perpendicular to, and running through the pyrazine ring of **4.7**. The bond lengths and bond angles of the bornane skeleton are similar to those of other camphor-fused aromatic heterocycles of this type (heterocycle fused to the C2-C3 bond of camphor).[203] An interesting consequence of the fusion of the bornane skeleton to the pyrazine ring is the lengthening of the C2-C3 bond, which has a distance of 1.405(2)Å. This is slightly longer than the C-C bond length of unsubstituted pyrazine [1.39Å],[204] which is presumably a consequence of the fused strained bornane ring-system.

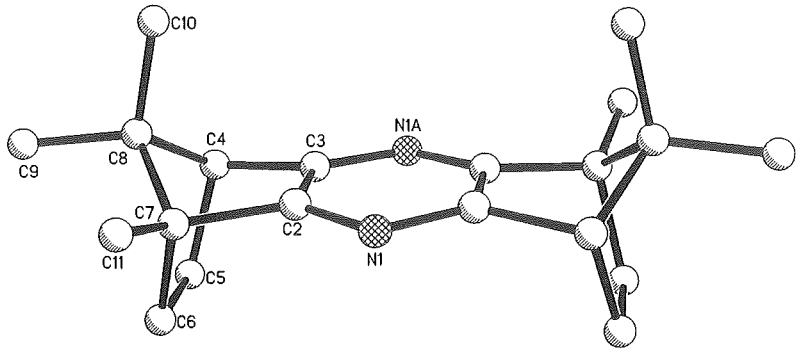


Figure 4.14 Perspective view of the structure of **4.7**. The hydrogen atoms have been omitted for clarity. Selected bond angles (Å) and bond lengths (°): N1-C2 1.356(2), N1A-C3 1.358(2), C2-C3 1.405(2), C2-C7 1.522(2), C3-C4 1.525(3), N1-C2-C3 124.2(2), N1-C2-C7 127.7(2), N1A-C3-C2 124.3(2), N1A-C3-C4 128.7(2), C3-C2-C7 107.7(12), C2-C3-C4 106.5(2).

The *anti*-isomer, **4.8**, crystallizes in the tetragonal space group $P4_12_12$, with half a molecule in the asymmetric unit. The structure of the molecule is shown in figure 4.15. As in the structure of **4.7** above, the absolute stereochemistry can be correctly assigned using

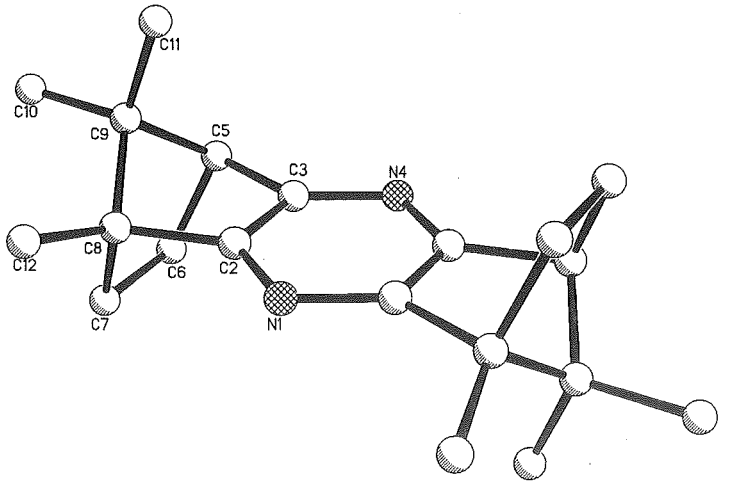


Figure 4.15 Perspective view of the structure of **4.8**, with the hydrogen atoms omitted for clarity. Selected bond lengths (Å) and bond angle (°): N1-C2 1.342(2), N4-C3 1.337(2), C2-C3 1.405(2), C2-C8 1.521(2), C3-C5 1.511(2), N1-C2-C3 124.0(2), N1-C2-C8 128.8(2), C3-C2-C8 107.1(2), N4-C3-C2 124.2(2), N4-C3-C5 129.1(2), C2-C3-C5 106.8(2)

the known stereochemistry of the starting material. The two halves of the structure are related to one another via a two-fold axis; however, unlike the structure of **4.7** above, the axis passes through the nitrogen atoms of the pyrazine ring. The bond lengths and bond angles of this compound are remarkably similar to those of **4.7** above, and are similar to those of other camphor-fused heterocycles of this type.[203]

4.3.2 Coordination chemistry of 4.7

The coordination chemistry of **4.7** was investigated by the formation of complexes with $AgNO_3$ (**4.9**) and CuI (**4.10**). The preparation of coordination complexes was also attempted with $Cu(NO_3)_2$, $Cd(NO_3)_2$, and $ZnBr_2$, but these failed to give any identifiable products. A space-filling representation of the structure of **4.7** indicated the relatively hindered environment of the nitrogen-donor atoms of the pyrazine ring.

The reaction of **4.7** with $AgNO_3$ in a 1:1 mixture of acetone-methanol gave colourless crystals of the silver nitrate complex, **4.9**. The complex analysed with a 1:1 metal-ligand stoichiometry. The complex was soluble in common solvents, and an NMR spectrum showed only uncoordinated ligand. The crystals formed were suitable for X-ray structure analysis.

The copper(I) iodide complex, **4.10**, was prepared by the reaction of **4.7** with CuI in acetonitrile. The yellow acetonitrile solution formed gave a mixture of large yellow crystals and colourless crystals after slow evaporation. The colourless crystals were identified as **4.7** only, while the yellow crystals of **4.10** were found to have an intriguing 4:3 metal-ligand stoichiometry. The crystals of **4.10** formed during the slow evaporation were suitable for single crystal structure analysis. An NMR spectrum of the complex in acetonitrile showed a set of peaks indicating all the molecules of **4.7** in the product are equivalent.

Crystal structure of **4.9**

The silver nitrate complex, **4.9**, crystallizes in the chiral orthorhombic space group $P2_12_12$. The asymmetric unit contains two molecules of **4.7**, two silver nitrates, two methanol and two water solvate molecules. The complex has a one-dimensional polymeric structure, with the polymer propagating along the two-fold screw axis. The nitrate counterions and solvate molecules occupy the spaces between the polymeric chains. The structure of **4.9** is shown in figure 4.16. The two molecules of **4.7** present in the structure

have similar bond lengths to those found in the X-ray structure of the free ligand described above, and will not be discussed further.

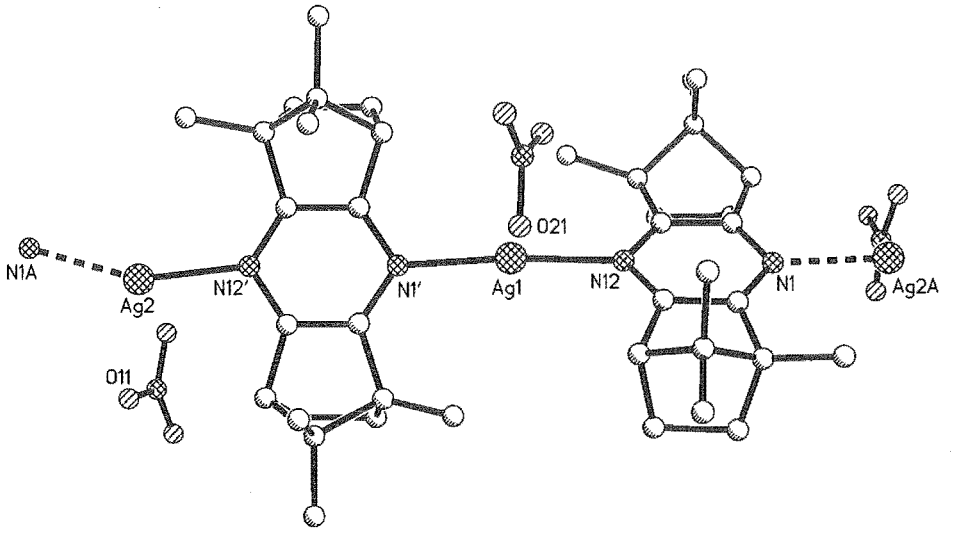


Figure 4.16 Perspective view of a section of the polymeric structure of **4.9**, showing the two different molecules of **4.7**, and the most significant contributing silver atom. The hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N1' 2.187(3), Ag1-N12 2.191(3), Ag2-N1A 2.256(5), Ag2-N12' 2.260(5), N1'-Ag1-N12 173.8(2), N1A-Ag2-N12' 156.9(2).

The two silver atoms are both coordinated by two molecules of **4.7**. Ag1 has a slightly distorted linear coordination geometry with Ag-N bond lengths of 2.191(3)Å and 2.187(3)Å. The meanplanes of the pyrazine rings are inclined at an angle of 49.9(1)°. Ag2 displays some positional disorder with a 3:1 ratio of occupancies, the major contributor is shown in figure 4.17. Ag2 has a slightly more distorted linear coordination geometry, with an N-Ag-N angle of 156.9(2)° compared to 173.8(2)° for Ag1. This distortion could be due to the close approach of one of the counterions [Ag2-O11 2.636(2)Å], which is closer than that of a counterion to the other silver atom [Ag1-O21 2.727(2)Å]. The nitrate counterion which approaches Ag2 is disordered over two sites, each of which lies on a two-fold rotation axis. The Ag-N distances to the disordered silver atom are slightly longer than those to Ag1, with bond lengths of 2.256(5)Å and 2.260(5)Å for the major contributing silver atom and 2.21(1)Å and 2.234(9)Å for the minor. The meanplanes of the pyrazine rings of the ligands coordinated to Ag2 are tilted at an angle of 129.1(1)°.

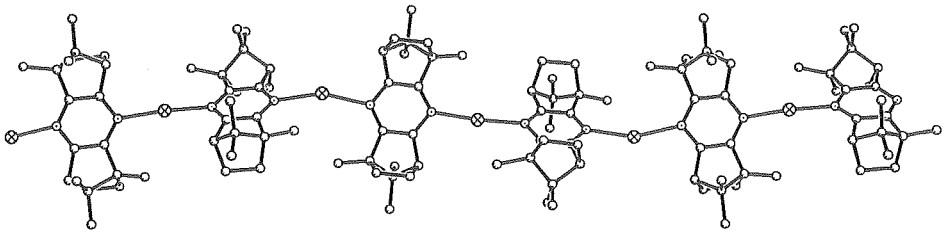


Figure 4.17 Perspective view of a section of the polymeric chain of **4.9**. The major contributing silver atoms are shown; hydrogen atoms, counterion and solvate molecules have been omitted for clarity.

The independent molecules of **4.7** align slightly differently, with the molecules coordinating Ag1 aligning head-to-tail, while the molecules coordinating Ag2 are aligned head-to-head. This gives a polymeric chain with pairs of head-to-tail units which are aligned head-to-head, as shown in figure 4.17. The silver atoms of the chain are separated by the pyrazine rings of the ligand molecules, with Ag···Ag distances of 7.292(4)Å and 7.313(4)Å. These distances are slightly longer than the corresponding silver-silver distance for the silver nitrate complex with pyrazine.[205] This is caused by the sterically demanding nature of the ligand **4.7**, which is also manifested by the relatively long Ag-N bond lengths and the two-coordinate nature of the silver atoms.

Crystal structure of **4.10**

The copper(I) iodide complex, **4.10**, crystallized in the chiral monoclinic space group C2. The asymmetric unit was found to contain a total of three independent molecules of **4.7** and four copper(I) iodides. The total of three ligands is comprised of two whole ligands, and two half ligands which lie on rotation axes. The complex has a one-dimensional polymeric structure, with the ligand molecules bridged by Cu_2I_2 units, as shown in figure 4.18. The two half-molecules of **4.7** are not coordinated to the copper atoms, and are involved in no significant interactions with the polymeric chains. Both the uncoordinated and coordinated molecules of **4.7** have bond lengths and angles similar to those found in the crystal structure of **4.7** above.

The four copper atoms of the structure are all three-coordinate, and form CuI_2Cu units which bridge the ligand molecules. This structure is similar to that reported for the copper(I) iodide complex of the structurally similar ligand phenazine, although this ligand

is achiral.[206] Both Cu_2I_2 units of the structure are subject to minor disorder with respect to the position of some of the atoms. This disorder results in a slight twisting in the Cu_2I_2 plane away from the plane of the pyrazine ring. The disorder is only minor, with the major contributing component having approximately 88% occupancy. The disorder is possibly a result of the sterically hindered environment of the donor-nitrogen atoms of **4.7**.

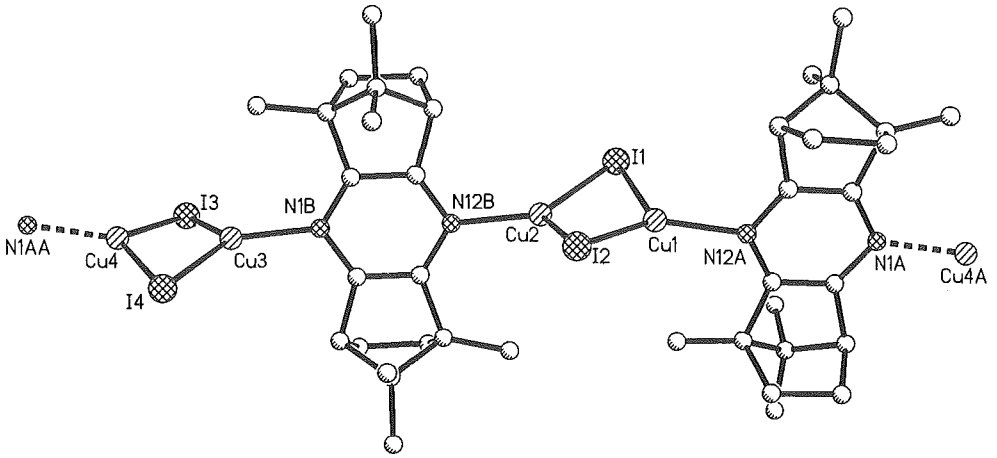


Figure 4.18 Perspective view of a section of the polymeric chain of **4.10**. The hydrogen atoms and uncoordinated molecules of **4.7** have been removed for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-N12A 2.022(4), Cu1-I2 2.555(2), Cu1-I1 2.602(2), Cu2-I1 2.554(2), Cu2-N12B 2.012(5), Cu2-I2 2.655(2), Cu3-N1B 2.003(4), Cu3-I3 2.580(2), Cu3-I4 2.587(4), Cu4-I3 2.605(3), Cu4-N1AA 2.002(5), Cu4-I4 2.572(3), N12A-Cu1-I2 131.3(2), N12A-Cu1-I1 109.9(2), I2-Cu1-I1 118.54(4), N12B-Cu2-I1 126.6(2), N12B-Cu2-I2 115.8(2), I1-Cu2-I2 116.60(6), N1B-Cu3-I3 121.1(2), N1B-Cu3-I4 118.2(2), I3-Cu3-I4 120.4(1), N1AA-Cu4-I4 120.9(3), N1AA-Cu4-I3 118.8(2), I4-Cu4-I3 120.0(2), Cu2-I1-Cu1 60.04(4), Cu1-I2-Cu2 59.33(4), Cu3-I3-Cu4 57.91(7), Cu4-I4-Cu3 58.22(9).

The copper atoms all have slightly distorted trigonal-planar coordination geometries, with the angles between the atoms coordinated to the copper atoms in the range 109.9(2) – 126.6(2)°. The Cu-N bond lengths lie between 2.002(5)Å and 2.022(5)Å, which are similar to other copper(I) iodide complexes with structures of this type. These complexes all involve sterically hindered nitrogen atoms, with the structures of 2,6-dimethylpyridine,[207] octahydrophenazine[208] and phenazine[206] all having ligands bridged by CuI_2Cu units with three-coordinate copper atoms. The structures of copper(I) iodide with less sterically hindered pyrazine rings involve four coordinate copper atoms, with discrete Cu_2I_2 units[106]

or polymeric $(CuI)_\infty$ structures.[105,209] It appears that the steric hindrance of **4.7** and the other ligands described above is manifest in the coordination number of the copper atom, rather than the metal-ligand distance. This is possibly due to the nature of the Cu_2I_2 rings, which separate the bulky ligands by a larger distance than is possible for a single atom, as in the silver nitrate complex **4.9**. Therefore, the steric bulk of the ligands is localised to the coordination environment of the copper atoms, which restricts the copper atom to a three-coordination geometry, and, as a consequence, stops more complex CuI motifs forming.[210]

The Cu_2I_2 units have Cu-I distances in the range 2.554(2) – 2.655(2)Å, which is similar to the three coordinate copper(I) iodide complexes described above. The Cu···Cu distances for the independent Cu_2I_2 rings are 2.510(3)Å and 2.580(2)Å, which are slightly smaller than the Cu···Cu distance for the structures described above. The Cu_2I_2 rings are not planar, with the iodide atoms distorted out of the plane to minimise the steric interaction with the adjacent methyl groups of the coordinated molecule of **4.3**. The rings are almost perpendicular to the pyrazine rings of the ligands, with angles between the meanplanes of the Cu_2I_2 rings and the pyrazine rings in the range 82.7(4)° – 102.3(4)°. The pyrazine rings of adjacent ligands are tilted at angles of 15.7(4)°.

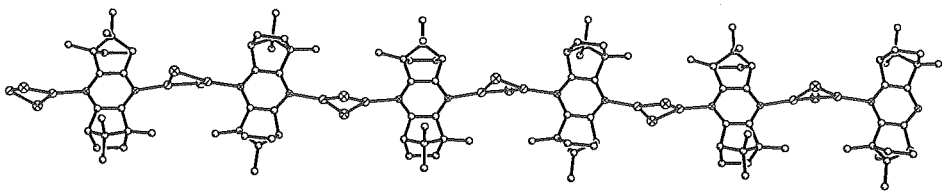


Figure 4.19 Perspective view of a section of the polymeric chain structure of **4.10**, showing the head-to-head alignment of the molecules of **4.7**. The hydrogen atoms and uncoordinated molecules of **4.7** have been removed for clarity.

The polymeric chains propagate along the *c*-axis of the unit cell, with the noncoordinated molecules of **4.7** occupying the spaces between the chains. A section of the polymeric chain is shown in figure 4.19. The pyrazine rings of the coordinated molecules bridge the copper atoms with Cu···Cu distances of 6.898(2)Å and 6.538(2)Å. These are slightly shorter than the distances of the silver nitrate structure, **4.9**, above, which is due to the shorter metal-ligand bond lengths. The distances between the nitrogen atoms across the Cu_2I_2 rings are 6.479(6)Å and 6.538(6)Å. The coordinated molecules of **4.7** align head-to-

head, so that methyl groups of adjacent molecules are close [C···C distances of 3.76(1)Å and 3.80(1)Å]. The head-to-head alignment is allowed by the increased distance between the molecules of **4.7**, due to the Cu_2I_2 units.

4.3.3 Coordination chemistry of 4.8

The coordination chemistry of **4.8** was investigated by the formation of a complex with $AgNO_3$ (**4.11**). Many attempts were made to form a complex with copper iodide, but all reactions tried gave only a mixture of colourless crystals, which were identified as crystals of **4.8**, and some unidentified material.

The silver nitrate complex, **4.11**, was prepared by the reaction of **4.8** with $AgNO_3$ in a 1:1 mixture of acetone-methanol. The complex analysed with a 1:1 metal-ligand stoichiometry. The crystals formed during the reaction were suitable for an X-ray structure analysis.

Crystal structure of **4.11**

The silver nitrate complex, **4.11**, crystallizes in the orthorhombic space group $P2_12_12_1$. The asymmetric unit contains two molecules of **4.8**, two silver nitrates and two disordered water solvate molecules. The one-dimensional polymeric structure of the complex is shown in figure 4.20. The two independent molecules of **4.8** present in the structure have bond lengths and angles similar to those found in the crystal structure of **4.8** (above). The nitrate counterions and disordered water solvate molecules occupy the spaces between the polymeric chains. The water molecules are disordered over three sites, each with approximately one-third occupancy. The water molecules are sufficiently far from the silver atoms and ligands to preclude any interactions. The molecules of **4.8** have similar bond lengths and angles to those found in the structure of the free ligand (above) and will not be discussed further.

The two independent silver atoms present in the structure are each coordinated by two molecules of **4.8**. The two silver atoms have similar geometries, and are both distorted from linear with N-Ag-N angles of 164.5(2)° and 167.5(2)°. Ag1 has Ag-N bond lengths of 2.195(4)Å and 2.199(4)Å, while Ag2 has bond lengths of 2.165(4)Å and 2.178(4)Å. The silver atoms are distorted from linearity towards the nitrate counterions, with two different nitrate counterions making close approaches [Ag1···O21 2.682(3)Å and Ag2···O11 2.678(3)Å]. The silver atoms display none of the disorder observed in the silver nitrate

complex of the isomeric molecule **4.7**, described above. As in the silver nitrate structure **4.9** above, the sterically hindered environment of the nitrogen donor atoms leads to the two-coordinate silver atoms.

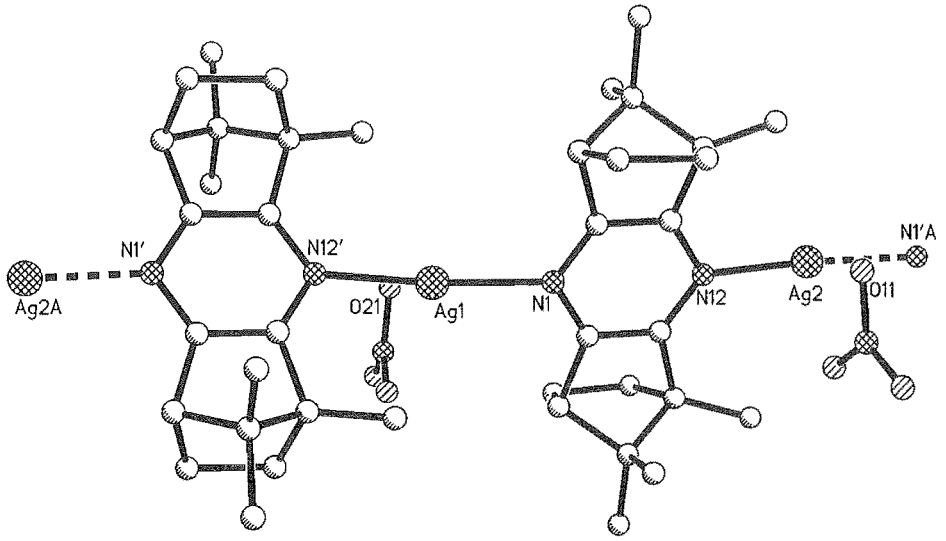


Figure 4.20 Perspective view of a section of the polymeric chain structure of **4.11**, showing the coordination environment of the silver atoms. The hydrogen atoms and disordered water solvate molecules have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ag1-N1 2.195(4), Ag1-N12' 2.199(4), Ag2-N1'A 2.165(4), Ag2-N12 2.178(4), N1-Ag1-N12' 164.5(2), N1'A-Ag2-N12 167.5(2).

The polymeric chains propagate along the *b*-axis of the unit cell. The pyrazine rings of the adjacent ligands on the chain bridge the silver atoms, with Ag···Ag distances of 7.186(2)Å and 7.191(2)Å. The pyrazine rings are tilted at an angle of 48.7(2)° to one another. The molecules of **4.8** align in a head-to-tail fashion, as shown in figure 4.21. The closest approach made by non-H atoms of adjacent ligand molecules of the chain occurs between C13 and C15', which are 3.833(6)Å apart.

The faithful head-to-tail alignment exemplifies the difference in the steric environments of the nitrogen donor atoms. Interestingly, this is not observed in the corresponding bond lengths, with the Ag-N bond lengths similar for the two sets of nitrogen donor atoms (more or less sterically hindered). This difference in environment of the donor atoms leads to the differences in alignment of the chains between the silver nitrate structure of the isomeric compounds **4.7** and **4.8**. The ligand **4.7** has symmetrical nitrogen atoms, and this gives a silver nitrate complex that has a polymeric structure with

alternating of head-to-head and head-to-tail units. The head-to-head arrangement is allowed by the tilting of adjacent ligands, with the closest approach between the head-to-head ligands being 4.09(1)Å between C11′ and C22 (adjacent methyl groups).

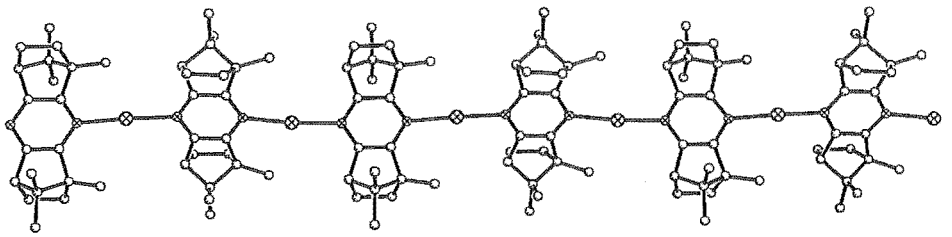


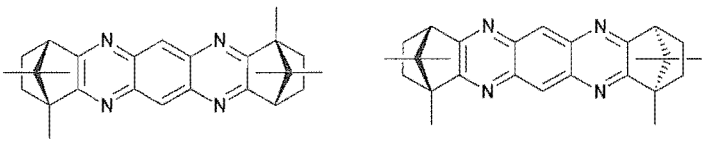
Figure 4.21 Perspective view of a section of the one-dimensional polymeric chain structure of **4.11**, showing the head-to-tail alignment of the molecules of **4.8**. The hydrogen atoms, nitrate counterions, and disordered water solvate molecules have been omitted for clarity.

The one-dimensional chiral coordination polymers with the ligands **4.7** and **4.8** illustrate the ability of these chiral molecules with sterically hindered donors to form such structures when combined with labile metal atoms. Furthermore, the comparison of **4.7**, with identical nitrogen environments, and **4.8**, with different nitrogen environments, shows the latter's ability to form directional coordination polymers. The use of steric environment to differentiate the donor atoms of a ligand to form directional polymers is a more subtle approach than has previously been used for the formation of directional polymers.

4.4 Tetraazaanthracene ligands with two fused camphors

The success of the *exo*-bridging ligand molecules **4.7** and **4.8** for the preparation of chiral coordination molecules led us to investigate the potential ligands *anti*-dicamphotetraazaanthracene (**4.12**) and *syn*-dicamphotetraazaanthracene (**4.13**) (fig 4.22) for this purpose. These molecules retain the two-fold symmetry of the ligand molecules **4.7** and **4.8**, while increasing the number of donor atoms. As above, the *syn*- and *anti*- prefixes refer to the relative side of the molecule that the bridgehead methyl groups occupy.

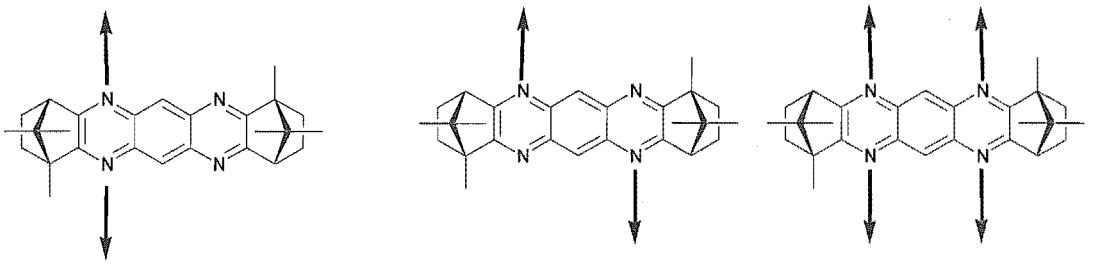
The four donor atoms of each molecule can be divided into two pairs, more hindered, with adjacent methyl groups, and less hindered, with adjacent hydrogen atoms. Due to the position of the two-fold axes in the ligands, the different donor atoms of **4.12** occur on the same side of the molecule, while those of **4.13** occur on opposite sides, as shown in figure 4.22. This means that for **4.12** to form a chiral polymer with directionality it has to bridge



4.12 **4.13**

Figure 4.22

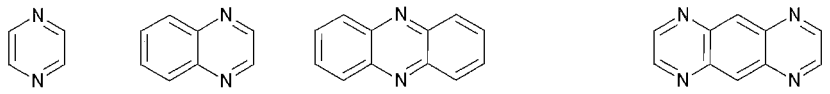
silver atoms through one of the fused pyrazine rings only. This is shown in figure 4.23. In contrast, any coordination polymers formed with **4.13** will be insensitive to the bridging mode of the ligand.



(a) (b)

Figure 4.23 Possible bridging modes of **4.12**, which will give rise to **(a)** directional polymers or **(b)** non-directional polymers.

Given the significance of linear *exo*-bridging ligands, such as pyrazine, quinoxaline and phenazine (fig 4.24(a)), particularly for the formation of coordination polymers,[33,182] it is perhaps interesting that the potential ligand 1,4,5,8-tetraazaanthracene (fig 4.24(b)) has never been used. The electronic properties of 1,4,5,8-tetraazaanthracene were calculated during a study into bridged porphyrins.[211] The ligand molecules **4.12** and **4.13** are camphor fused derivatives of 1,4,5,8-tetraazaanthracene, and their coordination chemistry with the labile metal atoms copper(I) and silver will be investigated.

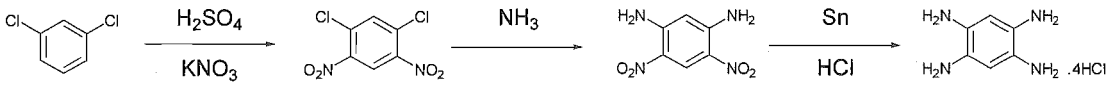


(a) (b)

Figure 4.24

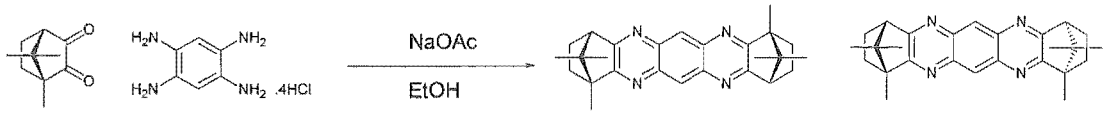
4.4.1 Ligand synthesis

The syntheses of the potential ligand molecules *anti*-dicamphotetraazaanthracene (**4.12**) and *syn*-dicamphotetraazaanthracene (**4.13**) required 1,2,4,5-tetraaminobenzene as a common synthon. This can be synthesised from *m*-dichlorobenzene, as shown in scheme 4.6. The method of Boyer and Burkies[212] was used for the synthesis of 1,3-diamino-4,6-dinitrobenzene, which involved the nitration of *m*-dichlorobenzene, followed by nucleophilic substitution of the product with ammonia at high temperatures in ethylene glycol. The reduction of 1,3-diamino-4,6-dinitrobenzene to 1,2,4,5-tetraaminobenzene was accomplished by the use of the method of Knobloch and Niedrich, which uses tin in concentrated hydrochloric acid as the reducing agent.[213] 1,2,4,5-tetraaminobenzene is isolated from the reaction mixture as a tetrahydrochloride salt, as the free base is prone to oxidation.[213]



Scheme 4.6

The potential ligand molecules, **4.12** and **4.13**, were synthesised by the reaction of 1,2,4,5-tetraaminobenzene and camphorquinone in dry ethanol with sodium acetate, as shown in scheme 4.7. The reaction was done under an argon atmosphere in an attempt to minimize oxidation of 1,2,4,5-tetraaminobenzene; despite these precautions a large amount of red material was obtained on completion of the reaction. After chromatography to remove unreacted camphorquinone a white solid was obtained, which was found to contain a 1:1 mixture of **4.12** and **4.13**. These observations were similar to those of Heckendorn, although he was unable to separate the mixture of isomers formed.[214] The separation of **4.12** and **4.13** was problematic, due to the similarity of the compounds, and involved repeated chromatography. The potential ligands **4.12** and **4.13** were eventually isolated in 15% and 14% yield after recrystallization.



4.12 4.13

Scheme 4.7

4.4.2 Complexes

The coordination chemistry of **4.12** and **4.13** was investigated by the formation of complexes with $AgNO_3$. The reactions of **4.12** and **4.13** with copper(I) iodide gave only a mixture of brown and white precipitates, respectively. The white precipitates were identified as containing only uncoordinated molecules of **4.12** or **4.13**, respectively.

The silver nitrate complexes, **4.14** and **4.15**, were prepared by the reactions of $AgNO_3$ with **4.12** and **4.13**, respectively, in a 1:1 mixture of acetone and methanol. The complexes both analysed with a 1:2 metal-ligand stoichiometry. Crystals suitable for X-ray structure analysis of **4.14** were isolated from the reaction mixture. Despite numerous attempts, no crystals of **4.15** could be isolated. No further analysis of this complex was undertaken.

Crystal structure of **4.14**

The silver nitrate complex, **4.14**, crystallizes in the orthorhombic space group $P2_12_12$. This is a chiral space group, and the asymmetric unit was found to contain half a molecule of **4.14**, one silver nitrate and some disordered solvate molecules. The complex has a one-dimensional polymeric structure, with the disordered solvate molecules and nitrate counterions occupying the spaces between the polymeric chains. The structure of **4.14** is shown in figure 4.25.

The silver atom is coordinated by two molecules of **4.14**, with Ag-N bond lengths of 2.257(5)Å and 2.277(5)Å. The silver atom displays a slight positional disorder over two sites, with the major site having 87% occupancy. The minor contributing silver atom has slightly shorter Ag-N bond lengths, and a less distorted linear coordination geometry, with an N-Ag-N angle of 168(2)°, as opposed to 158.8(3)° for the major contributing silver atom. The silver atom is probably distorted from linearity by the close approach of the nitrate counterion, with an Ag···O distance of 2.657(4)Å for the major contributing silver atom.

The polymeric chains propagate along the *a*-axis of the unit cell, with the two-fold axis running through the centroid of the central benzene ring of the ligand molecule. The ligand molecules each coordinate four silver atoms, with each of the ligands bridged by two silver

atoms. The polymeric chains are formed from 12-membered macrocycles, giving a 'train-track' structure, as shown in figure 4.26. The distance between the silver atoms across the ligand is 7.368(2)Å, while the distance between silver atoms on the same side of the ligand is 4.682(2)Å. The slightly longer Ag-N bond lengths and two coordinate silver atoms are possibly due to the sterically hindered nature of the nitrogen donor atoms of **4.12**.

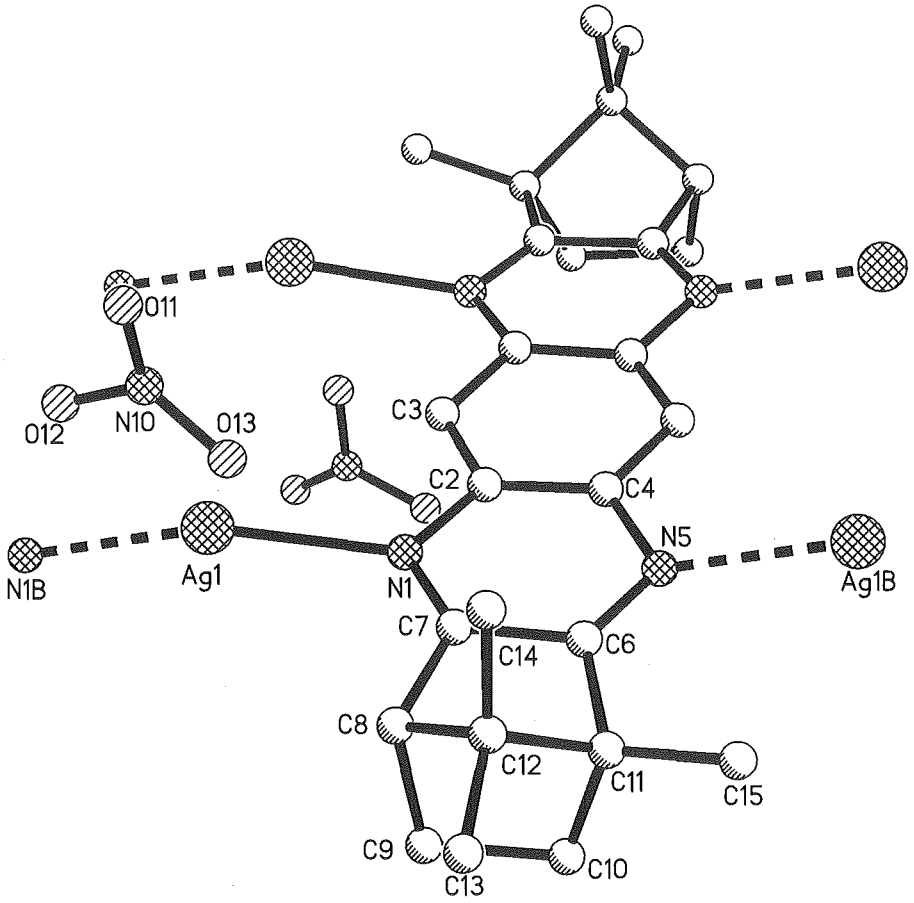


Figure 4.25 Perspective view of one molecule of **4.12** in the polymeric structure of **4.14**, with atomic numbering shown. The major contributing silver atoms are shown. The hydrogen atoms and solvate molecules have been omitted for clarity. Selected bond lengths and bond angles: Ag1-N1 2.257(5), Ag1B-N5 2.277(5), N1B-Ag1-N1 158.8(3).

The ligand molecules of the polymeric chains align in a head-to-tail fashion with the bridgehead methyl groups oriented towards the CH group. This arrangement allows the ligand molecules, which are restricted to the same plane by the two bridging silver atoms, to have the closest approach. This close approach gives a C···C distance of 3.65(1)Å, which

is similar to the distances between adjacent ligands found above. The Ag-N bond distances are different for the inequivalent nitrogen atoms, with the more sterically hindered nitrogen having a 0.02Å longer bond. The formation of the 'train-track' structure, with each ligand bridged to the next by two silver atoms, means that the chiral coordination polymer formed has no directionality.

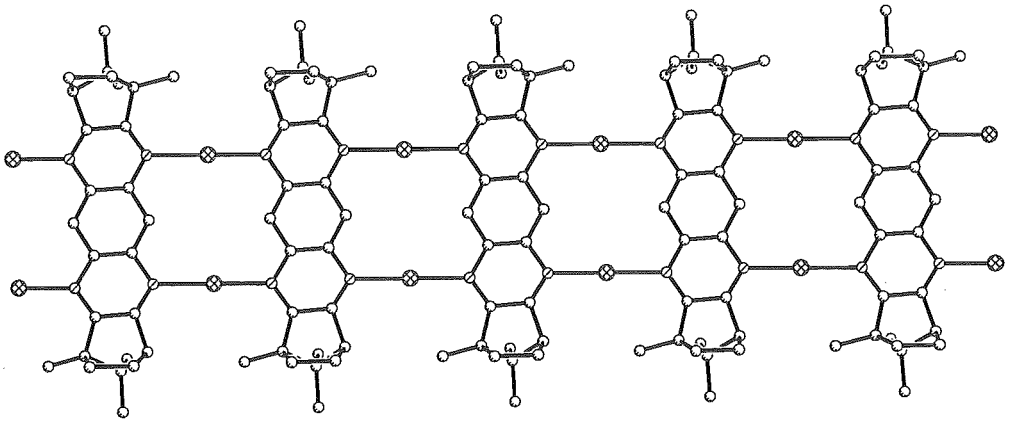


Figure 4.26 Perspective view of a section of one of the polymeric chains of **4.14**, showing the major contributing silver atoms only. The hydrogen atoms, nitrate counterions and solvate molecules have been omitted for clarity.

4.5 Conclusion

While the formation of chiral coordination compounds has been an area of extensive research, the preparation and study of chiral coordination polymers has been less studied. The preparation of chiral coordination polymers from labile metal atoms and enantiomerically pure ligands is a simple approach to this goal. Ligands based on monoterpenes can be conveniently prepared from commercially available enantiomerically pure starting materials. Chiral ligands formed by fusing linear *exo*-bridging heterocycles with camphor have allowed the successful preparation of a number of chiral polymers.

The ligand **4.1** has a single camphor moiety and forms a chiral 'ladder' polymer with silver nitrate. The difference in the environment of the nitrogens of **4.1** allowed the preparation of discrete mononuclear and tetranuclear complexes. The fusion of two

camphor moieties to a pyrazine gave the isomeric ligands **4.7** and **4.8**. These produced polymeric complexes with labile metal atoms. The extension of the heterocycle to include more donor atoms was achieved in the synthesis of the chiral molecules **4.12** and **4.13**. The silver nitrate complex of the former of these had an interesting 'train-track' one-dimensional polymeric structure.

The formation of directional polymers requires *exo*-bridging ligands with different donor sites. The ligands **4.1** and **4.8** effectively produced directional chiral coordination polymers due to the subtle differences in their donor atoms. The use of steric effects to differentiate the donor atoms is a new approach to the formation of directional polymers.

Chapter 5

Conclusion

5 Conclusion

This thesis has described the formation of a number of different ligands and the supramolecular chemistry of their coordination complexes. This approach to the formation of supramolecular assemblies utilizes metal-ligand coordinate bonds between N-heterocycles and metal atoms. The large number of metal atoms with varying preferred coordination numbers and geometries allows the simple preparation of a large range of metallosupramolecular assemblies. Ligands utilizing N-heterocycles have proven popular for the formation of metallosupramolecular assemblies as a consequence of their ease of synthesis and structural diversity.

This thesis involved the preparation of a number of nitrogen containing heterocycles, and the reaction of these with a range of different metal ions. The ligands chosen for these investigations can be divided into three types; *sym-biheterocycles*, *flexible ligands*, and ligands capable of forming *chiral coordination polymers*. The metallosupramolecular assemblies formed were investigated using X-ray crystallography to determine their three-dimensional structure.

The preparation of various 'multinodal' *sym*-biheterocycles allowed the production of a number of coordination complexes with interesting structural supramolecular chemistry. It was hoped that the mixture of binding modes available to these ligands would allow the formation of novel metallosupramolecular complexes. The structure of the complexes observed was found to depend on the conformation of the ligands. In none of these structures was the full number of donor atoms utilized. This could be due to the use of mainly labile metal atoms to form complexes, or steric hindrance of the donor atoms. The donor atoms available in the discrete complexes formed from these ligands could be used in the formation of mixed-metal metallosupramolecular assemblies.

Ligands containing flexible components allow the preparation of novel complexes as a consequence of their conformation flexibility. The ligands formed during this investigation comprise a rigid aromatic ring with appended heterocycles bridged by flexible linkers. The majority of the complexes isolated during this study had one-dimensional polymeric structures. This was probably due to the *exo*-bridging nature of the ligands used. Interestingly, the flexibility of the ligands was apparent more in the tilting of the heterocyclic rings than the conformation of the linker groups. This tilting allowed the formation of helical and undulating polymers. Ligands with three, rather than two,

heterocycles were able to produce interesting polymeric structures, with the ligands acting as three connector components.

The preparation of enantiomerically pure chiral ligands based on camphor allowed the successful isolation of a number of chiral coordination polymers. The one-dimensional polymeric structures formed with the labile metal atoms silver and copper(I). The reaction of these ligands with less labile metal atoms was unsuccessful, possibly due to the sterically crowded nitrogen atoms. The production of directional coordination polymers required that the nitrogen atoms were different, and these were formed in two cases.

The use of metal ions and anions capable of bridging metal atoms produced a number of interesting structures. This was most notable in the formation of a number of complexes using the halide salts of copper. Copper(I) iodide complexes of various ligands were prepared, with iodide bridging at least two metal atoms in all cases. Complexes were observed with discrete dinuclear, tetranuclear cube-like and polymeric stair-like copper(I) iodide motifs.

Secondary interactions between the components of the complexes were structurally significant in a number of the complexes characterized. The ligands used in these studies all involve nitrogen containing aromatic heterocycles, and such ligands can be involved in π-π interactions. These attractive interactions occurred in many of the crystal structures, with both face-to-face and edge-to-face observed. This was particularly apparent among the complexes involving *sym*-biheterocycles and flexible ligands. The large bulk of the fused camphor ligands makes these interactions less likely for these molecules.

Hydrogen bonding interactions between the components of the complexes were also observed. The hydrogen atoms of the ligands molecules were all attached to carbon atoms, and are less likely to be involved in hydrogen bonding. However, the inclusion of solvent, coordinated molecules, and the use of anions containing hydrogen bonding acceptor atoms, such as nitrate, allowed the formation of structurally significant hydrogen bonds in a number of complexes.

Thus, the twenty six ligands prepared for this thesis were investigated with the aim of the formation of interesting metallosupramolecular assemblies. The formation of a variety of complexes allowed this, and the structures of the compounds formed were investigated using X-ray crystallography. The diverse range of complexes formed exemplifies the large variety of metallosupramolecular assemblies that can be formed by the reaction of simple ligands with metal atoms.

Chapter 6

Experimental

6 Experimental

6.1 General Experimental

NMR spectra were recorded on Varian Unity 300 or Varian INOVA 500 spectrometers at 23°C with a 3 mm probe and operating at 300MHz or 500MHz for ^{1}H, respectively, and 75MHz for ^{13}C. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced relative to the internal standard Me_4Si and those recorded in deuterated dimethyl sulfoxide and acetonitrile were referenced against the solvent signals at 2.5 and 2.0 ppm, respectively. ^{13}C NMR spectra recorded in $CDCl_3$ were referenced against the solvent signal at 77.0 ppm and those recorded in dimethyl sulfoxide and acetonitrile were referenced against the solvent signals at 36.8 and 117.7 ppm, respectively. When required, ^{1}H nOe, 1-D TOCSY, COSY, GHSQC and GHMBC experiments were performed using the standard pulse sequences available with the Varian INOVA 500 system. Unless otherwise stated the value for the chemical shift is given to the centre of the multiplet.

Mass spectra (EI and FAB) were recorded using a Kratos MS80RFA mass spectrometer with a Mach 3 data system. Electron Impact (EI) spectra were obtained at 70 eV with a source temperature of 250°C. Fast Atom Bombardment (FAB) spectra were acquired in a nitrobenzyl alcohol matrix using an Iontech ZN11NF FAB gun operated at 8 KV and 2 mA. Electrospray mass spectra were recorded using a Micromass LCT TOF mass spectrometer, with a probe operating at 3200 V and cone voltage of 30 V. Samples were dissolved in 1:1 acetonitrile/water, and spectra acquired using source and desolvation temperatures of 80°C and 150°C, respectively.

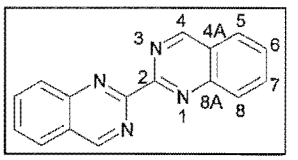
Melting points were determined using an Electrothermal melting point apparatus and are uncorrected. The Campbell microanalytical laboratory, University of Otago, Dunedin performed elemental analyses.

Unless otherwise stated reagents were obtained from commercial sources and used as received. Solvents were purified by standard literature procedures. The following compounds were prepared using literature procedures: N,N'-(di-o-formylphenyl)oxanilide,[50] 3-bromoquinoline,[215] 1-methyl-1,5-napthyridin-2(1H)-one,[55] nickel(II) bistriphenylphosphine bromide,[216] 2-chloroquinoxaline,[103] 1,4-benzenedimethanol,[217] dihydrocamphopyrazine,[218] camphorquinone,[186] 1,2,4,5-tetraaminobenzene[213] and dihydrocamphopyrazine.[193]

6.2 Ligands

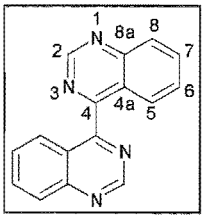
6.2.1 Biheterocycles

2,2'-Biquinazoline, **2.1.**



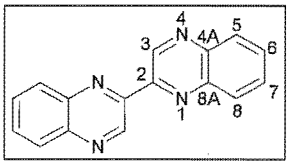
N,N'-(Di-o-formylphenyl)oxanilide (3.03g, 0.01mol) and saturated ethanolic ammonia (25ml) were placed in a sealed tube and heated to 140°C for 23hrs. The yellow solid that formed was filtered off and recrystallized from butan-1-ol. Yield 2.06g (78%). M.p. 286-287°C (lit.[50] 285-286°C). ^{1}H NMR (300MHz, $CDCl_3$): δ 9.75 (2H, s, H4), 8.43 (2H, d, H8), 8.07 (2H, d, H5), 8.03 (2H, t, H6), 7.77 (2H, t, H7).

4,4'-Biquinazoline, **2.2.**



Quinazoline (0.279g, 2.1mmol) was stirred with NaCN (1.11g, 23mmol) in water (10ml) at 20°C for 21hrs. The yellow solid was filtered off and dried. This solid was stirred with MnO_2 (1.56g) in benzene (150mL) at R.T. for 21hrs. The solution was then filtered and the volume reduced *in vacuo* to 30mls. White crystals formed on standing at 0°C. Yield 0.24g (43%). M.p. 239-240°C (lit.[50] 246-247°C). ^{1}H NMR (300MHz, $CDCl_3$): 9.56(2H, s, H2), 8.23 (2H, d, H8), 8.01 (2H, t, H7), 7.93 (2H, d, H5), 7.61 (2H, t, H6).

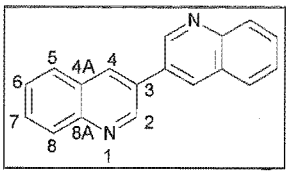
2,2'-Biquinoxaline, **2.3.**



Quinoxaline hydrochloride (1.39g, 8.3mmol) in dry DMF (10mls) with N,N-dimethylaniline (1ml) was heated to 140°C for 1hr. The reaction mixture was allowed to cool and 140ml of 2M ammonia solution was added. The precipitate that formed was filtered off, dried and purified by sublimation. Yield 0.65g (61%). M.p. 269-271°C (lit.[51] 273-274°C). ^{1}H NMR (300MHz, $CDCl_3$): δ 10.13 (2H, s, H3), 8.25 (4H, m, H5,8), 7.88 (4H, m, H6,7).

3-3'-Biquinoline, **2.4.**

3-Bromoquinoline (1.72g, 8.2mmol), K_2CO_3 (1.20, 8.6mmol), $Pd(OAc)_2$ (0.091g, 0.4mmol), and ^{n}Bu$_4$NI (1.48g, 4.0mmol) were stirred in DMF (10mls) at 115°C for 5mins.

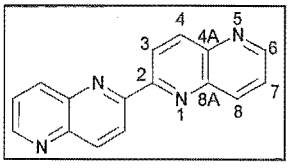


Isopropyl alcohol was added and the mixture stirred at 115°C for 23hrs. The solution was added to 25mls H_2O and extracted with Et_2O (2x50mls). The organic phase was washed (25mls H_2O), dried (Na_2SO_4) and the residue purified by chromatography (15g silica, pet ether) to give a pale yellow solid. Yield 0.59g (56%). M.p. 269-270°C (lit.[54] 270°C). ^{1}H NMR (500MHz, $CDCl_3$): δ 9.30 (2H, s, H2), 8.40 (2H, s, H4), 8.18 (2H, d, H8), 7.95 (2H, d, H5), 7.78 (2H, t, H6), 7.64 (2H, t, H7).

2-Chloro-1,5-naphthyridine.

1-Methyl-1,5-naphthyridine(1H)-2-dione (0.96g, 6.0mmol) and phosphorus pentachloride (1.25g, 6.0mmol) were refluxed in phosphorus oxychloride (50mls) for 24hrs. The solvent was evaporated *in vacuo* to give a brown solid. This was suspended in water (75mls) and neutralized ($NaHCO_3$). This suspension was extracted with $CHCl_3$ (2x75mls) and the organic phase washed (2x20mls H_2O, 20mls brine), dried (Na_2SO_4) and the solvent evaporated *in vacuo*. The solid formed was recrystallized from 1:1 pet-ether/ethyl acetate to give 2-chloro-1,5-naphthyridine as an orange solid. Yield 0.58g (59%). M.p. 109-111°C (lit.[219] 112°). ^{1}H NMR (500MHz, $CDCl_3$): 8.98 (H, dd, H6), 8.34 (2H, m, H8,H4), 7.63 (2H, m, H3,H7).

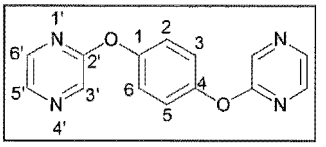
2,2'-Bi-1,5-naphthyridine, **2.5**.



Nickel(II) bistriphenylphosphine bromide (0.79g, 1.1mmol), zinc powder (0.45g, 6.9mmol), and tetraethylammonium iodide (0.90g, 3.4mmol) were stirred at R.T. in dry THF (15mls) under argon for 30 mins. 2-Chloro-1,5-naphthyridine (0.57g, 3.5mmol) was added in dry THF (10mls) and the mixture stirred at 50°C for 22hrs under argon. The mixture was poured onto 100mls 2M NH_3 and extracted with $CHCl_3$ (2x75mls). The organic phase was washed (H_2O, 50mls), dried (Na_2SO_4) and the solvent removed *in vacuo* to give a brown solid. This was purified via chromatography (10g Silica, EtOAc), and the product recrystallized (1:1 pet ether/EtOAc) to give a yellow solid. Yield 0.10g (22%). M.p. 275-276°C (lit.[53] 282-284°C) ^{1}H NMR (300MHz, $CDCl_3$): 9.08 (2H, d, H3), 9.03 (2H, d, H6), 8.58 (2H, d, H4), 8.55 (2H, d, H8), 7.71 (2H, dd, H7).

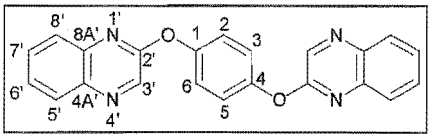
6.2.2 Flexible Ligands

1,4-Bis(2-pyrazinyloxy)benzene, **3.1**.



Hydroquinone (0.355g, 3.2mmol), 2-chloropyrazine (0.5ml, 4.7mmol) and potassium carbonate (1.11g, 8.0mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 17hrs. The resulting suspension was poured onto 10% NaOH soln. (20mls) and the precipitate filtered off and washed with H_2O (2x2mls). The resulting white powder was recrystallized from n-heptane to give **3.1** as a white crystalline solid. Yield 0.523g (44%). M.p. 197°C. Anal. Found: C, 63.19; H, 3.90; N, 20.74. Calc. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. ^{1}H NMR (300MHz, $CDCl_3$): δ 8.46 (2H, s, H3′), 8.29 (2H, s, H6′), 8.13 (2H, s, H5′), 7.24 (4H, s, H2,H3,H5,H6). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.03, C2′; 149.99, C1,C4; 141.00, C6′; 138.66, C5′; 135.91, C3′; 122.55, C2,C3,C5,C6. EI-MS: Found M^+ 266.0811, $C_{14}H_{10}N_4O_2$ requires M^+ 266.0804.

1,4-Bis(2-quinoxalinyloxy)benzene, **3.2**.

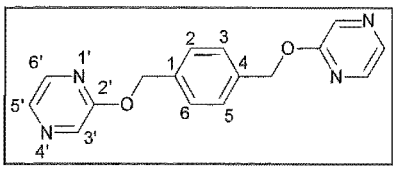


Hydroquinone (0.701g, 6.4mmol), 2-chloroquinoxaline (1.70g, 0.10mmol) and potassium carbonate (2.06g, 15mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 15hrs. The resulting suspension was poured onto 10% NaOH soln. (20mls), the precipitate was filtered off and washed with H_2O (2x2mls). The resulting yellow powder was recrystallized from acetone/water to give **3.2** as a yellow powder. Yield 1.28g (68%). M.p. 226-227°C. Anal. Found: C, 71.52; H, 3.72; N, 15.45. Calc. for $C_{22}H_{14}N_4O_2$: C, 71.25; H, 3.94; N, 15.11. ^{1}H NMR (300MHz, $CDCl_3$): δ 8.75 (2H, s, H3′), 8.09 (2H, d, H8′), 7.84 (2H, d, H5′), 7.67 (4H, m, H6′,H7′), 7.40 (4H, s, H2,H3,H5,H6). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.86, C1′; 149.78, C1,C4; 137.86, C4A′; 137.70, C8A′; 139.17, C3′; 130.52, C7′; 128.96, C5′; 127.69, C8′; 127.58, C6′; 122.61, C2,C3,C5,C6. EI-MS: Found M^+ 366.1117, $C_{22}H_{14}N_4O_2$ requires M^+ 366.1123.

1,4-Bis(2-pyrazinyloxymethyl)benzene, **3.13**

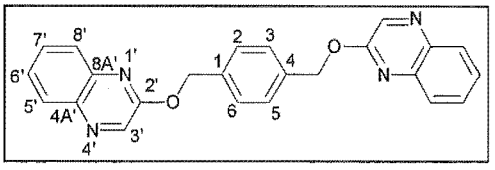
A solution of 1,4-benzenedimethanol (0.287g, 2.1mmol) in THF (5mls) was added

dropwise to a suspension of NaH (50% in paraffin, 0.28g, 4.1mmol) in THF (5mls) at 0°C under nitrogen. The mixture was stirred for 30mins at R.T. and 2-chloropyrazine (0.478g, 4.2mmol) was added dropwise in THF (5mls). After 15hrs at reflux the solution was poured onto 40mls ice/water slurry and extracted with $CHCl_3$ (2x75mls). The organic phase was dried (Na_2SO_4) and the solvent evaporated to give a yellow crystalline solid, which was recrystallized from pet ether/EtOAc (1:1) to give **3.13** as a yellow crystalline solid. Yield 0.457g (75%). M.p. 126–128°C. Anal. Found: C, 65.14; H, 4.83; N, 19.00. Calc. for $C_{16}H_{14}N_4O_2$: C, 65.30; H, 4.79; N, 19.04. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.29 (2H, s, H3′), 8.14 (2H, d, H5′), 7.10 (2H, m, H6′), 7.48 (4H, m, H2,H3,H5,H6), 5.40 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 159.89, C1′; 140.45, C6′; 136.77, C3′; 136.32, C1,C4; 128.30, C5′; 108.49, C2,C3,C5,C6; 67.50, CH_2. EI-MS: Found M^+ 292.1168, $C_{16}H_{14}N_4O_2$ requires M^+ 292.1190.

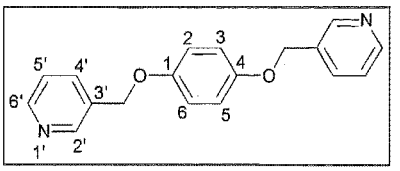


1,4-Bis(2-Quinolxalyloxymethyl)benzene, **3.14.**

A solution of 1,4-benzenedimethanol (0.284g, 2.1mmol) in THF (5mls) was added dropwise to a suspension of NaH (50% in paraffin, 0.28g, 5.8mmol) in THF (10mls) at 0°C under nitrogen. The mixture was stirred at R.T. for 30mins and 2-chloroquinoxaline (0.685g, 4.2mmol) was added dropwise in THF (5mls). After 22hrs at reflux the solution was poured onto 40mls ice/water slurry and extracted with $CHCl_3$ (2x75mls). The organic phase was dried (Na_2SO_4) and the solvent evaporated to give a yellow solid, which was recrystallized from pet ether/EtOAc (1:1) to give **3.14** as a yellow crystalline powder. Yield 0.593g (73%). M.p. 178–179 °C. Anal. Found: C, 72.26; H, 4.67; N, 14.04. Calc. for $C_{24}H_{18}N_4O_2.¼H_2O$: C, 72.54; H, 4.66 N, 14.13. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.53 (2H, s, H3′), 8.03 (2H, d, H8′), 7.87 (2H, d, H5′), 7.69 (2H, t, H6′), 7.59 (6H, m, H7′,H2,H3,H5,H6), 5.57 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.96, C2′; 140.20, C4A′; 139.57, C3′; 138.98, C8A′; 136.31, C1,C4; 130.18, C7′; 128.97, C5′; 128.63, C2,C3,C5,C6; 127.18, C8′; 126.67, C6′; 67.76, CCH_2. EI-MS: Found M^+ 394.1430, $C_{16}H_{14}N_4O_2$ requires M^+ 394.1440.

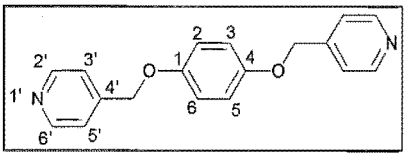


1,4-Bis(3-pyridylmethoxy)benzene, **3.25.**



Hydroquinone (0.582g, 5.3mmol), 3-chloromethylpyridine hydrochloride (1.71g, 10.4mmol) and potassium carbonate (3.41g, 25mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 26hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with $CHCl_3$ (2x75mls). The organic extracts were dried (Na_2SO_4) and reduced *in vacuo* to a black solid. Flash chromatography (20g silica, 10:90 MeOH/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.25** as a white crystalline solid. Yield 0.60g (39%). M.p. 142–143°C. Anal. Found: C, 73.66; H, 5.74; N, 9.76. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.67 (2H, s, H2′), 8.58 (2H, d, H6′), 7.70 (2H, d, H4′), 7.32 (2H, m, H5′), 6.92 (4H, s, H2,H3,H5,H6), 5.04 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 152.82, C1,C4; 149.34, C2′; 148.92, C6′; 135.18, C4′; 132.56, C3′; 123.42, C5′; 115.85, C2,C3,C5,C6; 68.14, CH_2. EI-MS: Found M^+ 292.1218, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.

1,4-Bis(4-pyridylmethoxy)benzene, **3.26.**

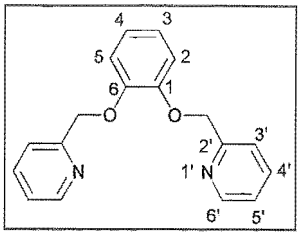


Hydroquinone (0.216g, 1.96mmol), 4-chloromethylpyridine hydrochloride (0.657g, 4.0mmol) and potassium carbonate (1.86g, 13.5mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 17hrs. The resulting suspension was poured onto H_2O (40mls) and extracted with $CHCl_3$ (2x75mls). The organic extracts were dried (Na_2SO_4) and reduced *in vacuo* to a yellow liquid. Recrystallization from 1:1 pet ether/EtOAc gave **3.26** as yellow needles. Yield 0.361g (63%). M.p. 167–168°C. Anal. Found: C, 73.92; H, 5.68; N, 9.73. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.61 (4H, m, H2′,H6′), 7.34 (4H, d, H3′,H5′), 6.89 (4H, s, H2,H3,H5,H6), 5.05 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 158.72, C1,C4; 149.95, C2′,C6′; 146.28, C4′; 121.43, C3′,C5′; 115.80, C2,C3, C5,C6; 68.74, CH_2. ES-MS: Found M^+ 292.1217, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.

1,2-Bis(2-pyridylmethoxy)benzene, **3.40.**

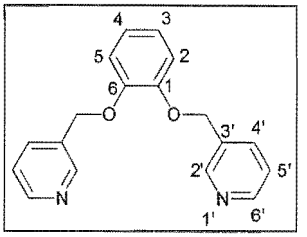
Catechol (0.67g, 6.1mmol), 2-chloromethylpyridine hydrochloride (2.31g, 14.1mmol) and

potassium carbonate (4.10g, 30mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 24hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were washed (2x50mls H_2O, 50mls brine), dried (Na_2SO_4) and reduced *in vacuo* to a brown solid. Flash chromatography (20g silica, EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.40** as a white crystalline solid. Yield 0.85g (48%). M.p. 59-60°C. Anal. Found: C, 73.65; H, 5.35; N, 9.65. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.60 (2H, s, H6′), 7.70 (2H, t, H4′), 7.62 (2H, d, H3′), 7.21 (2H, m, H5′), 6.92 (4H, m, H2,H3,H4,H5), 5.32 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.33, C2′; 148.91, C6′; 148.22, C1,C6; 136.70, C4′; 122.43, C5′; 121.59, C3,C4; 121.10, C3′; 114.30, C2,C5; 71.46, CH_2. EI-MS: Found M^+ 292.1217, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.



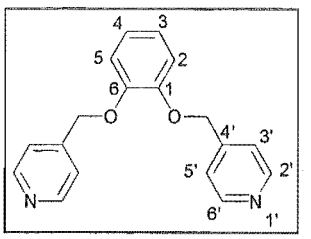
1,2-Bis(3-pyridylmethoxy)benzene, **3.41**.

Catechol (0.56g, 5.1mmol), 3-chloromethylpyridine hydrochloride (1.72g, 10.4mmol) and potassium carbonate (3.61g, 26mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 27hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were combined, washed (2x50mls H_2O, 50mls brine), dried (Na_2SO_4) and reduced *in vacuo* to a brown solid. Flash chromatography (20g silica, 90:10 EtOAc/MeOH) and recrystallization from 1:1 pet ether/EtOAc gave **3.41** as a white crystalline solid. Yield 0.36g (24%). M.p. 76-77°C. Anal. Found: C, 73.77; H, 5.58; N, 9.72. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.67 (2H, s, H2′), 8.57 (2H, d, H6′), 7.78 (2H, d, H4′), 7.29 (2H, m, H5′). 6.96 (4H, m, H2,H3,H4,H5), 5.14 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 149.33, C2′; 148.84, C6′; 148.56, C1,C6; 135.17, C4′; 132.58, C3′; 123.44, C5′; 122.14 C3,C4; 115.85, C2,C5; 68.89, CH_2. EI-MS: Found M^+ 292.1219, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.



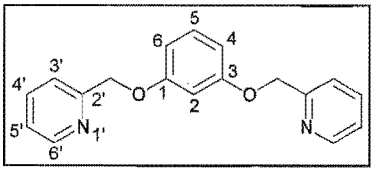
1,2-Bis(4-pyridylmethoxy)benzene, **3.42**.

Catechol (0.60g, 5.5mmol), 4-chloromethylpyridine hydrochloride (1.81g, 11.0mmol) and



potassium carbonate (3.41g, 25mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 21hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were washed (2x50mls H_2O, 50mls brine) dried (Na_2SO_4) and reduced *in vacuo* to a brown solid. Flash chromatography (20g silica, 90:10 EtOAc/MeOH) and recrystallization from 1:1 pet ether/EtOAc gave **3.42** as a white crystalline solid. Yield 0.35g (22%). M.p. 101-102°C. Anal. Found: C, 74.12; H, 5.59; N, 9.69. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.61 (4H, s, H2′,H6′), 7.37 (4H, d, H3′,H5′), 6.92 (4H, m, H2,H3,H4,H5), 5.18 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 149.86, C2′,C6′; 148.18, C1,6; 146.22, C4′; 122.03, C3′,5′; 121.29, C3,C4; 114.66, C2,C5; 69.25, CH_2. EI-MS: Found M^+ 292.1219, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.

1,3-Bis(2-pyridylmethoxy)benzene, **3.55.**

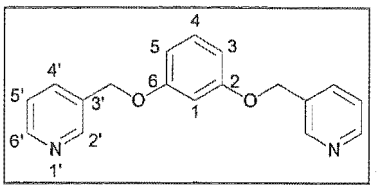


Resorcinol (0.61g, 5.5mmol), 2-chloromethylpyridine hydrochloride (2.01g, 12.1mmol) and potassium carbonate (3.81g, 26mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 30hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were washed (2x50mls H_2O, 50mls brine) dried (Na_2SO_4) and reduced *in vacuo* to a black solid. Flash chromatography (20g silica, 10:90 pet ether/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.55** as a white crystalline solid. Yield 1.21g (75%). M.p. 51-52°C. Anal. Found: C, 74.16; H, 5.67; N, 9.85. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.59 (2H, d, H6′), 7.71 (2H, t, H4′), 7.50 (2H, d, H3′), 7.22 (2H, m, H5′), 7.17 (H, d, H5), 6.62 (H, s, H2), 6.60 (2H, d, H4,H6), 5.18 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 159.30, C1,C3; 156.71, C2′; 148.81, C6′; 136.58, C4′; 129.78, C5; 122.37, C3′; 121.03, C5′; 107.23, C4,C6; 101.95 C2; 70.24, CH_2. EI-MS: Found M^+ 292.1216, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.

1,3-Bis(3-pyridylmethoxy)benzene, **3.56.**

Resorcinol (0.59g, 5.3mmol), 3-chloromethylpyridine hydrochloride (1.78g, 10.8mmol) and potassium carbonate (2.97g, 22mmol) were stirred at 100°C in dry DMF (10mls)

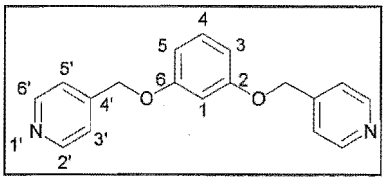
under nitrogen for 24hrs. The resulting suspension was poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were washed (2x50mls H_2O, 50mls brine) dried (Na_2SO_4) and reduced *in vacuo* to



a brown oil. Flash chromatography (20g silica, EtOAc) gave **3.56** as a pale yellow solid. Yield 0.67g (43%). M.p. 79-80°C. Anal. Found: C, 73.73; H, 5.42; N, 9.48. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.68 (2H, s, H2′), 8.60 (2H, d, H6′), 7.77 (2H, d, H4′), 7.33 (2H, m, H5′), 7.23 (H, m, H1), 6.62 (3H, m, H3,H4,H5,H6), 5.06 (4H, s, HCH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 159.59, C2,C6; 149.40, C2′; 148.90, C6′; 135.25, C4′; 132.33, C3′; 130.15, C4; 123.49, C5′; 107.56, C3,C5; 102.25, C1; 67.52, CH_2. EI-MS: Found M^+ 292.1221, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1212.

1,3-Bis(4-pyridylmethoxy)benzene, **3.57.**

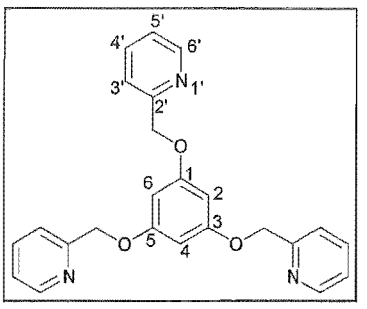
Resorcinol (0.61g, 5.5mmol), 4-chloromethylpyridine hydrochloride (1.81g, 11.1mmol) and potassium carbonate (3.81g, 26mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 30hrs. The resulting suspension was



poured onto H_2O (50mls) and extracted with CH_2Cl_2 (2x75mls). The organic extracts were washed (2x50mls H_2O, 50mls brine) dried (Na_2SO_4) and reduced *in vacuo* to a black solid. Flash chromatography (20g silica, 10:90 pet ether/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.77** as a white crystalline solid. Yield 0.64g (40%). M.p. 96-97°C. Anal. Found: C, 73.74; H, 5.51; N, 9.72. Calc. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.61 (4H, d, H2′,H6′), 7.34 (4H, d, H3′,H5′), 7.21 (H, t, H4), 6.58 (H, m, H1,H3,H5), 5.06 (4H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 159.36, C1,C6; 149.89, C2′,C6′; 145.95, C4′; 130.18, C5; 121.38, C3′,C5′; 107.52, C4,C6; 102.25, C2; 68.14, CH_2. EI-MS: Found M^+ 292.1218, $C_{18}H_{16}N_2O_2$ requires M^+ 292.1213.

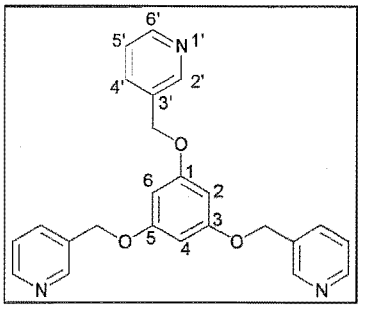
1,3,5-Tris(2-pyridylmethoxy)benzene, **3.70.**

Phloroglucinol (0.69g, 5.5mmol), 2-chloromethylpyridine hydrochloride (2.69g, 16.4mmol) and potassium carbonate (4.91g, 35.5mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 22hrs. The resulting suspension was poured onto H_2O (200ml) and extracted with Et_2O (3x100mls). The organic phase was washed with H_2O (2x50mls),



dried (Na_2SO_4) and the solvent evaporated to give an off white solid. Flash chromatography (40g alumina, 20:80 pet ether/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.70** as a white crystalline solid. Yield 0.86g (39%). M.p. 126-127°C. Anal. Found: C, 72.31; H, 5.43; N, 10.81. Calc. for $C_{24}H_{21}N_3O_3$: C, 72.17; H, 5.30; N, 10.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.59 (3H, s, H6′), 7.70 (3H, d, H4′), 7.48 (3H, d, H3′), 7.22 (3H, m, H5′), 6.30 (3H, s, H2,H4,H6), 5.15 (6H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.12, C1,C3,C5; 156.71, C2′; 149.03, C6′; 136.58, C4′; 122.43, C5′; 121.10, C3′; 94.94, C2,C4,C6; 70.50, CH_2. EI-MS: Found M^+ 399.15935, $C_{24}H_{21}N_3O_3$ requires M^+ 399.15829.

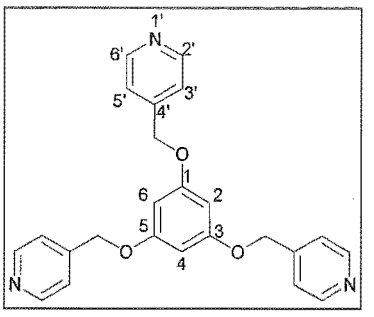
1,3,5-Tris(3-pyridylmethoxy)benzene, **3.71**.



Phluoroglucinol dihydrate (0.50g, 3.1mmol), 3-chloromethylpyridine hydrochloride (1.57g, 9.6mmol) and potassium carbonate (7.16g, 51.8mmol) were stirred at 100°C in dry DMF (10mls) under nitrogen for 18hrs. The resulting suspension was poured onto H_2O (200ml) and extracted with Et_2O (2x200ml). The organic phase was dried (Na_2SO_4) and the solvent evaporated to give an off-white solid. Flash chromatography (20g silica, 20:80 MeOH/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.71** as a white crystalline solid. Yield 0.43g (36%). M.p. 168°C. Anal. Found: C, 72.31; H, 5.35; N, 10.47. Calc. for $C_{24}H_{21}N_3O_3$: C, 72.17; H, 5.30; N, 10.58. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.67 (3H, s, H2′), 8.67 (3H, d, H6′), 8.60 (3H, d, H4′), 7.75 (3H, m, H5′), 6.26 (3H, s, H2,H4,H6), 5.04 (6H, s, CH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.32, C1,C3,C5; 149.53, C2′; 148.98, C6′; 135.26, C4′; 132.11, C3′; 123.50, C5′; 95.07, C2,C4,C6; 67.66, CH_2. EI-MS: Found M^+ 399.1593, $C_{24}H_{21}N_3O_3$ requires M^+ 399.1583.

1,3,5-Tris(4-pyridylmethoxy)benzene, **3.72**.

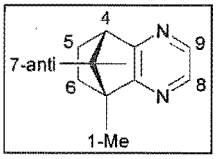
Phloroglucinol (0.63g, 5.0mmol), 4-chloromethylpyridine hydrochloride (2.96g, 17.5mmol) and potassium carbonate (5.06g, 36.6mmol) were stirred at 120°C in dry DMF (10mls) under nitrogen for 22hrs. The resulting suspension was poured onto H_2O (200ml) and extracted with Et_2O (3x100ml). The organic phase was washed with H_2O (2x50mls),



dried (Na_2SO_4) and the solvent evaporated to give an off white solid. Flash chromatography (40g alumina, 20:80 pet ether/EtOAc) and recrystallization from 1:1 pet ether/EtOAc gave **3.72** as a white crystalline solid. Yield 0.77g (39%). M.p. 171-172°C. Anal. Found: C, 71.86; H, 5.72; N, 10.04. Calc. for $C_{24}H_{18}N_4O_2.¼H_2O$: C, 71.86; H, 5.72; N, 10.43. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.61 (6H, d, H2′,H6′), 7.31 (6H, d, H3′,H5′), 6.21 (3H, s, H2,H4,H6), 5.03 (6H, s, HCH_2). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.13, C1,C3,C5; 149.99, C2′,C6′; 145.70, C4′; 121.40, C3′,C5′; 95.13, C2,C4,C6; 68.23, CH_2. EI-MS: Found M^+ 399.1601, $C_{24}H_{21}N_3O_3$ requires M^+ 399.1583.

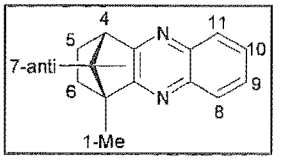
6.2.3 Chiral Ligands

Camphopyrazine, **4.1.**



Dihydrocamphopyrazine (4.35g, 22.8mmol) and potassium hydroxide (3.21g, 57.2mmol) were stirred in dry ethanol (50mls) at 50°C as oxygen was bubbled through the solution for 24hrs. The solvent was removed *in vacuo* and the residue extracted with CH_2Cl_2 (2x50mls). The organic phase was washed with water (25mls), dried (Na_2SO_4) and the solvent removed *in vavuo* to give a colourless crystalline solid. This was recrystallized from 1:1 pet ether/EtOAc to give **4.1** as colouless crystals. Yield 3.21g (75%). M.p. 59°C (lit.[220] 52-55°C). ^{1}H NMR (300MHz, $CDCl_3$): δ 8.12 (2H, m, H8,H9), 2.94 (1H, d, H4), 2.21 (1H, m, $H6_{exo}$), 1.96 (1H, m, $H5_{exo}$), 1.32 (3H, s, H1-Me), 1.27 (2H, dd, $H5_{endo}$, $H6_{endo}$), 1.03 (3H, s, H7-*anti*), 0.57 (3H, s, H7-*syn*). ^{1}H NMR (300MHz, CD_3CN): δ 8.16 (1H, m, H8,H9), 2.94 (1H, d, H4), 2.21 (1H, m, $H6_{exo}$), 2.04 (1H, m, $H5_{exo}$), 1.34 (3H, s, H1-Me), 1.24 (2H, dd, $H5_{endo}$, $H6_{endo}$), 1.09 (3H, s, H7-*anti*), 0.59 (3H, s, H7-*syn*).

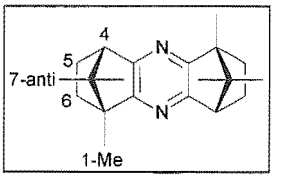
Camphoquinoxaline, **4.2.**



Camphoquinone (1.66g, 10.0mmol) and freshly sublimed *o*-phenylenediamine (1.09g, 10.1mmol) were refluxed in acetic acid (20ml) for 4 hours. The reaction mixture was neutralised with NaOH and extracted with ether (2x50ml). The organic phase was dried to give a yellow

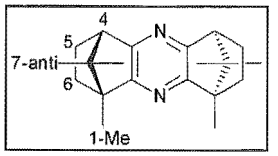
oil, which solidified on standing. This was purified by column chromatography (20g silica, 1:3 pet ether/EtOAc) to give **4.2** as a colourless crystalline solid. Yield 1.41g (59%). M.p. 76°C (lit.[183] 78°C). ^{1}H NMR (300MHz, $CDCl_3$): δ 8.05 (2H, m, H8,H11), 7.61 (2H, m, H9,H10), 3.05 (1H, d, H4), 2.30 (1H, m, $H6_{exo}$), 2.06 (1H, m, $H5_{exo}$), 1.44 (3H, s, H1-Me), 1.43 (2H, dd, $H5_{endo}$, $H6_{endo}$), 1.12 (3H, s, H7-*anti*), 0.63 (3H, s, H7-*syn*).

Anti-dicamphopyrazine, **4.7**.



Dihydro-*anti*-dicamphopyrazine (1.67g, 5.6mmol) and anhydrous ferric chloride (3.011g, 18.5mmol) were refluxed in dry ethanol (50ml) for 21hrs. The mixture was added to H_2O (50mls) and extracted with ether (3x50mls). The organic phase was dried (Na_2SO_4) to give a white solid. This was recrystallized from EtOH/H_2O to give **4.7** as white crystals. Yield 1.13g (68%). M.p. 160-161°C (lit.[195]159°C). ^{1}H NMR (300MHz, $CDCl_3$): δ 2.92 (2H, d, H4), 2.14 (2H, m, $H6_{exo}$), 1.90 (2H, m, $H5_{exo}$), 1.33 (6H, s, H1-Me), 1.22 (4H, dd, $H5_{endo}$, $H6_{endo}$), 0.98 (6H, s, H7-*anti*), 0.58 (6H, s, H7-*syn*). ^{1}H NMR (300MHz, CD_3CN): δ 2.96 (2H, d, H4), 2.29 (2H, m, $H6_{exo}$), 2.04 (2H, m, $H5_{exo}$), 1.37 (6H, s, H1-Me), 1.23 (4H, dd, $H5_{endo}$, $H6_{endo}$), 1.10 (6H, s, H7-*anti*), 0.67 (6H, s, H7-*syn*).

Syn-dicamphopyrazine, **4.8**.

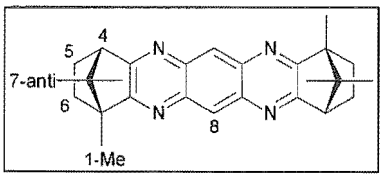


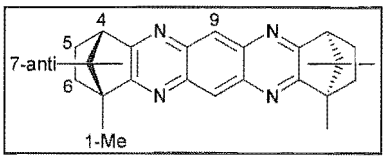
Camphorquinone (0.83g 5.0mmol), ammonium acetate (3.97g, 51.5mmol) and hexamethylenetetramine (7.01g, 50.0mmol) were refluxed in dry acetic acid under nitrogen for 20hrs. The mixture was added to water (100mls), neutralized (NaOH) and extracted with ether (2x75mls). The organic phase was washed with water (50mls), dried (Na_2SO_4) and the solvent evaporated *in vacuo* to give a yellow solid. Flash chromatography (10g silica, 1:1 pet ether/EtOAc) and recrystallization form 1:1 acetone/water gave **4.8** as a white crystalline solid. Yield 0.16g (22%). M.p. 202-203°C (lit.[202] 204-205°C). ^{1}H NMR (500MHz, $CDCl_3$): δ 2.85 (2H, d, H4), 2.15 (2H, m, $H6_{exo}$), 1.88 (2H, m, $H5_{exo}$), 1.32 (6H, s, H1-Me), 1.21 (4H, dd, $H5_{endo}$, $H6_{endo}$), 0.98 (6H, s, H7-*anti*), 0.54 (6H, s, H7-*syn*).

Anti-dicamphotetraazaanthracene, **4.12** and *Syn*-dicamphotetraazaanthracene, **4.13**.

1,2,4,5-Tetraaminobenzene (2.11g, 7.4mmol), camphorquinone (2.35g, 14.1mmol) and sodium acetate (2.62g 32mmol) were refluxed in dry ethanol under argon for 40hrs. The

ethanol was evaporated *in vacuo* and the red solid extracted with $CHCl_3$ (2x75mls). This was washed (2x50mls), dried (Na_2SO_4) and the solvent evaporated *in vacuo*. The yellow solid was chromatographed (20g silica, 1:1 pet ether/EtOAc) to remove unreacted camphorquinone. The remaining off white solid was a 1:1 mixture of **4.12** and **4.13**. Yield 0.99g. These were separated by repeated chromatography (20g silica 3:1 pet ether/EtOAc) to give **4.12** and **4.13** as white solids which were recrystallized from 1:1 pet ether ethyl acetate. **4.12**: Yield 0.41g (15%). M.p. >300°C. Anal. Found: C, 78.36; H, 7.59; N, 14.06. Calc. for $C_{26}H_{30}N_4$: C, 78.34 ; H, 7.37; N, 14.04. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.65 (2H, s, H9), 3.10 (2H, d, H4), 2.34 (2H, m, $H6_{exo}$), 2.09 (2H, m, $H5_{exo}$), 1.48 (4H, dd, $H5_{endo}$, $H6_{endo}$), 1.47 (6H, s, H1-Me), 1.15 (6H, s, H7-*anti*), 0.67 (6H, s, H7-*syn*). EI-MS: Found M^+ 398.2480, $C_{26}H_{30}N_4$ requires M^+ 398.2471. **4.13**: Yield 0.39g (14%). M.p. >300°C. ^{1}H NMR (500MHz, $CDCl_3$): δ 8.70 (1H, s, H8), 8.60 (1H, s, H9), 3.11 (2H, d, H4), 2.34 (2H, m, $H6_{exo}$), 2.09 (2H, m, $H5_{exo}$), 1.48 (4H, dd, $H5_{endo}$, $H6_{endo}$), 1.47 (6H, s, H1-Me), 1.15 (6H, s, H7-*anti*), 0.66 (6H, s, H7-*syn*). Anal. Found: C, 78.32; H, 7.62; N, 14.12. Calc. for $C_{26}H_{30}N_4$: C, 78.34 ; H, 7.37; N, 14.06. EI-MS: Found M^+ 398.2463, $C_{26}H_{30}N_4$ requires M^+ 398.2471.





6.3 Complexes of *Sym*-Biheterocycles

6.3.1 Preparation of complexes with 2.1.

With silver nitrate, *viz* **2.6.**

Reaction of **2.1** (12.6mg, 0.049mmol) in methanol with silver nitrate (17.0mg, 0.10mmol) in methanol gave a yellow precipitate immediately. Yield 15.1mg (48%). M.p. >250°(dec.). Anal. Found: C, 31.51; H, 2.47; N, 12.97. Calc. for $C_{16}H_{10}N_4AgNO_3.H_2O.MeOH$ C, 31.39; H, 2.47; N, 13.08.

With palladium chloride, *viz* **2.7.**

Reaction of **2.1** (13.0mg, 0.05mmol) dissolved in hot acetone and a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow crystalline solid immediately. Yield

19.0 mg (95%). M.p. >300°C (dec.). Anal. Found: C, 43.69; H, 2.40; N, 12.17. Calc. for $C_{16}H_{10}N_4PdCl_2.½MeOH$: C, 43.88; H, 2.68; N, 12.41. ^1H NMR (500MHz, DMSO): δ 10.30 (2H, s, H4), 8.73 (2H, d), 8.51 (4H, m), 8.16 (2H, t, H). Single crystals were grown by immersion of a Li_2PdCl_4 solution in a solution of **2.1**.

With copper(II) chloride, *viz* **2.8.**

Reaction of **2.1** (12.8mg, 0.05mmol) in methanol with copper(II) chloride (17.1mg, 0.10mmol) in methanol gave a green precipitate. Yield 20.7mg. M.p. 279°C. Anal. Found: C, 48.67; H, 3.13; N, 15.18. Calc. for $C_{16}H_{10}N_4CuCl_2.1½DMF$ C, 48.98; H, 3.43; N, 14.87. Crystals suitable for X-ray structure analysis were grown from diffusion of acetonitrile into a DMF solution of the complex.

With copper(I) iodide, *viz* **2.9.**

Reaction of **2.1** (12.9mg, 0.05mmol) in acetonitrile with copper(I) iodide (19.7mg, 0.10mmol) in acetonitrile gave a black precipitate. Yield 21.0mg (66%). M.p. > 280°C. Anal. Found: C, 30.54; H, 1.45; N, 8.26. Calc. for $C_{16}H_{10}N_4Cu_2I_2$ C, 30.29 H, 1.69; N, 8.56.

With cadmium nitrate, *viz* **2.10.**

Reaction of **2.1** (12.8mg, 0.05mmol) dissolved in dichloromethane with cadmium nitrate (31.4mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A colourless crystalline solid appeared on cooling. Yield 24.1mg (71%). Anal. Found: C, 25.50; H, 1.67; N, 14.87 Calc. for $C_{16}H_{10}N_8O_{12}Cd_2.2¼H_2O$: C, 25.22; H, 2.05; N, 15.26. Crystals suitable for X-ray diffraction were obtained by recrystallization from 1:1 $MeOH/H_2O$.

6.3.2 Preparation of complexes with 2.2.

With silver nitrate, *viz* **2.11**

Reaction of **2.2** (12.8mg, 0.05mmol) in acetone with silver nitrate (17.2mg, 0.10mmol) in methanol gave a white precipitate immediately. Yield 8.1mg (34%). M.p. >250°(dec.). Anal. Found: C, 38.03; H, 2.27; N, 14.61. Calc. for $C_{32}H_{20}N_{11}O_9Ag_3.1/3(CH_3)_2CO$ C, 38.35; H, 2.27; N, 14.47.

With palladium chloride, *viz* **2.12.**

Reaction of **2.2** (12.8mg, 0.050mmol) in acetonitrile with a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow solid. Yield 17.4mg (72%). M.p. >330°C. Anal. Found: C, 44.29; H, 3.12; N, 5.59. Calc. for $C_{16}H_{10}N_4PdCl_2.3H_2O$ C, 44.59; H, 3.32; N, 5.77.

With copper(II) chloride, *viz* **2.13.**

Reaction of **2.2** (12.8mg, 0.05mmol) in acetonitrile with copper(II) chloride (17.4mg, 0.10mmol) in methanol gave a green solution. Small green crystals appeared on standing overnight. Yield 11.1mg (53%). M.p. >200° (dec.). Anal. Found: C, 49.91; H, 2.90; N, 14.68. Calc. for $C_{16}H_{10}N_4CuCl_2.½CH_3CN.1/3(CH_3)_2CO$ C, 49.97; H, 3.15; N, 14.57.

6.3.3 **Preparation of complexes with 2.3.**

With silver nitrate, *viz* **2.14.**

Reaction of **2.3** (13.3mg, 0.051mmol) in dichloromethane (10ml) with silver nitrate (17.4mg, 0.10mmol) in methanol (10ml) gave an orange solution. Orange crystals suitable for X-ray structure analysis were obtained from the solution on standing. Yield 16.2mg (74%). M.p. 199-201°C. Anal. Found C, 44.75; H, 2.47; N, 15.99; Calc for $C_{16}H_{10}N_5O_3Ag$: C, 44.88; H, 2.37; N, 16.36.

With palladium chloride, *viz* **2.15.**

Reaction of **2.3** (12.8mg, 0.050mmol) in methanol with a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a brown-black solid. Yield 8.1mg. M.p. >330°C. No consistent elemental analysis results could be obtained.

With copper(II) chloride, *viz* **2.16.**

Reaction of **2.3** (13.3mg, 0.052mmol) with copper(II) chloride (18.5mg, 0.107mmol) in methanol gave a green black crystalline solid. Yield 18.5mg (84.6%). M.p. >350°C. Anal. Found: C, 46.94; H, 3.27; N, 12.65. Calc. for $C_{16}H_{10}N_4CuCl_2.MeOH.½H_2O$: C, 47.07; H,

3.59; N, 12.92. Crystals suitable for X-ray crystal structure analysis were obtained by layering a methanol solution of copper(II) chloride onto a dichloromethane solution of **2.3**.

With copper(I) iodide, *viz* **2.17**.

Reaction of **2.3** (12.9mg, 0.05mmol) in acetone with copper iodide (19.7mg, 0.10mmol) in acetonitrile gave a black precipitate. Yield 19.4mg (65%). M.p. >300°C. Anal. Found: C, 27.14; H, 1.34; N, 7.57. Calc. for $C_{32}H_{20}N_8Cu_5I_5.¼(CH_3)_2CO$: C, 27.17 H, 1.37; N, 7.53. Recrystallization of this black solid from DMSO gave deep red square plates.

With cadmium chloride, *viz* **2.18**.

Reaction of **2.3** (13.3mg, 0.05mmol) dissolved in hot dichloromethane with cadmium chloride (17.4mg, 0.10mmol) dissolved in hot methanol gave white precipitate immediately. The precipitate was filtered off and washed (2x2ml MeOH). Yield 15.3mg (69%). M.p. 278-280°C. Anal. Found: C, 43.59; H, 2.51; N, 12.61; Calc. for $C_{16}H_{10}N_4CdCl_2$: C, 43.52; H, 2.28; N, 12.69.

With copper(I) bistriphenylphosphine nitrate, *viz* **2.19**.

Reaction of **2.3** (12.7mg, 0.049mmol) in methanol (10ml) with copper(I) bistriphenylphosphine nitrate (65.0mg, 0.10mmol) in methanol (10ml) gave a red solution. Large red crystals were obtained on slow evaporation of this solution. Yield 32.6mg (73%). M.p. 210-212°C. Anal. Found C, 68.19; H, 4.61; N, 7.46; Calc for $C_{52}H_{40}N_5O_3P_2Cu.MeOH$: C, 68.21; H, 4.58; N, 7.58.

6.3.4 Preparation of complexes with 2.4.

With silver nitrate, *viz* **2.20**.

Reaction of **2.4** (12.8mg, 0.050mmol) in methanol with silver nitrate (17.4mg, 0.10mmol) in methanol formed a white precipitate on standing for 10 minutes. Yield 25.7mg. This product turned into a black precipitate within minutes that could not be identified.

With palladium chloride, *viz* **2.21.**

Reaction of **2.4** (12.8mg, 0.050mmol) in methanol with a methanolic solution of Li_2PdCl_4 gave an orange solid immediately. Yield 17.4mg (72%). M.p. >330°C. Anal. Found: C, 44.29; H, 3.12; N, 5.59. Calc. for $C_{18}H_{12}N_2PdCl_2.3H_2O$ C, 44.59; H, 3.32; N, 5.77.

With copper(II) nitrate, *viz* **2.22.**

Reaction of **2.4** (12.0mg, 0.047mmol) dissolved in hot dichloromethane with copper(II) nitrate (12.6mg, 0.052mmol) dissolved in hot methanol gave a green solution. A green precipitate appeared on standing. Yield 12.9mg (61%). M.p. >250°C (dec.). Anal. Found: C, 47.74; H, 2.89; N, 12.37. Calc. for $C_{18}H_{12}N_4O_6Cu.½H_2O$: C, 47.97; H, 2.65; N, 12.38.

With copper(I) iodide, *viz* **2.23.**

Reaction of **2.4** (12.9mg, 0.05mmol) in acetonitrile with copper(I) iodide (19.7mg, 0.10mmol) in acetonitrile gave a yellow precipitate. Yield 21.2mg (73%). M.p. > 280°C. Anal. Found: C, 33.37; H, 1.67; N, 4.33. Calc. for $C_{54}H_{36}N_6Cu_5I_5$ C, 33.38 H, 1.87; N, 4.33.

With cadmium chloride, *viz* **2.24.**

Reaction of **2.4** (12.8mg, 0.05mmol) dissolved in hot acetone with cadmium chloride (11.9mg, 0.05mmol) dissolved in hot methanol gave a white precipitate immediately. The precipitate was filtered off and washed (1x2ml MeOH). Yield 11.3mg (61%). M.p. >300°C. Anal. Found: C, 42.86; H, 3.19; N, 4.21 Calc. for $C_{36}H_{24}N_4Cd_3Cl_6.(CH_3)_2CO.CH_3OH$: C, 42.52; H, 3.57; N, 4.51.

6.3.5 Preparation of complexes with 2.5.

With silver tetrafluoroborate, *viz* **2.25.**

Reaction of **2.5** (13.0mg, 0.05mmol) dissolved in hot acetonitrile with silver tetrafluoroborate (20.5mg, 0.11mmol) dissolved in hot acetonitrile gave a light yellow solution. Crystals suitable for X-ray diffration were obtained from pentane diffusion into

the reaction mixture. Yield 11.19mg (29%). M.p. >200°C (dec.). Anal. Found: C, 38.59; H, 2.19; N, 11.82. Calc. for $C_{24}H_{15}N_4Ag_2B_2F_8.CH_3CN$: C, 38.16; H, 2.22; N, 11.99.

With palladium chloride, *viz* **2.26**

Reaction of **2.5** (12.0mg, 0.047mmol) in methanol with a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow solid. Yield 13.0mg (42%). M.p. >300°C (dec.). Anal. Found: C, 31.49; H, 1.74; N, 9.14. Calc. for $C_{16}H_{10}N_4Pd_2Cl_4$: C, 31.35; H, 1.64; N, 9.14.

With copper(II) nitrate, *viz* **2.27.**

Reaction of **2.5** (13.0mg, 0.05mmol) dissolved in hot acetonitrile with copper(II) nitrate (25.1mg, 0.10mmol) dissolved in hot acetonitrile gave a green solution. Crystals suitable for X-ray diffraction were obtained after 4 hours. Yield 15.7mg (70%). M.p. >270°C (dec.). Anal. Found: C, 42.93; H, 2.43; N, 19.00. Calc. for $C_{16}H_{10}N_6O_6Cu$: C, 43.10; H, 2.43; N, 18.85.

6.4 Flexible Ligand Complexes (-O-)

6.4.1 Preparation of complexes with 3.1.

With silver nitrate, *viz* **3.3.**

Reaction of **3.1** (13.3mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.4mg, 0.10mmol) dissolved in hot methanol gave a brown precipitate immediately. The precipitate was filtered off and washed (2x2ml MeOH). Yield 21.9mg (61%). M.p. 278-280°C. Anal. Found: C, 29.88; H, 1.78; N, 11.96 Calc. for $C_{14}H_{10}N_6O_8Ag_2.2/3(CH_3)_2CO.¼CH_2Cl_2$: C, 29.54; H, 2.18; N, 12.34.

With palladium chloride, *viz* **3.5.**

Reaction of **3.1** with Li_2PdCl_4 in methanol gave a black precipitate that could not be identified.

With copper(II) nitrate, *viz* **3.7**.

Reaction of **3.1** (13.4mg, 0.05mmol) dissolved in hot acetone with copper(II) nitrate (24.4mg, 0.10mmol) dissolved in hot methanol gave a blue precipitate immediately. The precipitate was filtered off and washed (2x2ml MeOH). Yield 25.3mg (56%). M.p. >280°C (dec.). Anal. Found: C, 19.40; H, 1.94; N, 14.05 Calc. for $C_{14}H_{10}N_{10}O_{21}Cu_3.CH_2Cl_2.$ ½MeOH.$2H_2O$: C, 19.25; H, 2.08; N, 14.95.

With copper(I) iodide, *viz* **3.9**.

Reaction of **3.1** (13.2mg, 0.05mmol) in acetonitrile with copper(I) iodide (19.2mg, 0.10mmol) in acetonitrile gave a yellow precipitate. Yield 18.1mg (55%) M.p. >320°C (dec.). Anal. Found: C, 25.42; H, 1.39 N, 8.34. Calc. for $C_{16}H_{10}N_4O_2Cu_2I_2.½H_2O$: C, 25.63 H, 1.69; N, 8.54. Crystals suitable for single crystal structure analysis were prepared by carefully layering a solution of copper(I) iodide in acetonitrile onto a dichloromethane solution of **3.1**.

With cadmium chloride, *viz* **3.11**.

Reaction of **3.1** (13.5mg, 0.051mmol) dissolved in hot dichloromethane with cadmium chloride (24.2mg, 0.11mmol) dissolved in hot methanol gave a white precipitate immediately. The precipitate was filtered off and washed (2x2ml MeOH). Yield 24.1mg (70%). M.p. >250°C (dec.). Anal. Found: C, 24.70; H, 1.84; N, 7.95 Calc. for $C_{14}H_{10}N_4O_2Cd_2Cl_4.2½H_2O$: C, 24.80; H, 2.23; N, 8.26.

6.4.2 **Preparation of complexes with 3.2.**

With silver nitrate, *viz* **3.4**.

Reaction of **3.2** (17.9mg, 0.048mmol) dissolved in hot acetone with silver nitrate (18.1mg, 0.10mmol) dissolved in hot methanol gave a white precipitate immediately. Yield 14.4mg (64%). M.p. 226-228°C. Anal. Found: C, 49.93; H, 3.03; N, 12.39 Calc. for $C_{22}H_{14}N_5O_5Ag.½(CH_3)_2CO$: C, 50.11; H, 3.20; N, 12.39.

With palladium chloride, *viz* **3.6**.

Reaction of **3.2** (19.6mg, 0.05mmol) dissolved in hot acetonitrile and a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow solid immediately. Yield 23.1 mg (73%). M.p. >300°C (dec.). Anal. Found: C, 47.90; H, 3.37; N, 9.12. Calc. for $C_{22}H_{14}N_4O_2PdCl_2.1½MeOH$: C, 47.70; H, 3.41; N, 9.47. Insoluble in common NMR solvents.

With copper(II) nitrate, *viz* **3.8**

Reaction of **3.2** (18.1mg, 0.049mmol) dissolved in hot dichloromethane with copper(II) nitrate (18.1mg, 0.10mmol) dissolved in hot methanol gave a blue solution. A blue precipitate was obtained on standing. Yield 21.1mg (77%). M.p. >300°C (dec.). Anal. Found: C, 47.40; H, 2.55; N, 15.17 Calc. for $C_{22}H_{14}N_6O_8Cu$: C, 47.95; H, 2.70; N, 14.83.

With copper(I) iodide, *viz* **3.10**.

Reaction of **3.2** (18.1mg, 0.05mmol) in acetonitrile with copper(I) iodide (19.2mg, 0.10mmol) in acetonitrile gave a yellow precipitate. Yield 24.8mg (67%). M.p. 300°C (dec.). Anal. Found: C, 35.36; H, 1.89 N, 7.50. Calc. for $C_{22}H_{14}N_4O_2Cu_2I_2$: C, 35.39 H, 1.75; N, 7.27. Crystals suitable for single crystal structure analysis were prepared by carefully layering a solution of copper(I) iodide in acetonitrile onto a dichloromethane solution of **3.2**.

With cadmium chloride, *viz* **3.12**.

Reaction of **3.2** (18.2mg, 0.05mmol) dissolved in hot methanol with cadmium nitrate (24.1mg, 0.11mmol) dissolved in hot methanol gave a colourless solution. A white crystalline solid appeared overnight. Yield 20.6mg (75%). M.p. >280°C (dec.). Anal. Found: C, 47.25; H, 2.41; N, 9.87. Calc. for $C_{22}H_{14}N_4O_2CdCl_2.½H_2O$: C, 47.30; H, 2.71; N, 10.03.

6.4.3 Preparation of complexes with 3.13.

With silver nitrate, *viz* **3.15**.

Reaction of **3.13** (14.6mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.5mg,

0.10mmol) dissolved in hot methanol gave a colourless solution. An off-white solid appeared on standing for 15 mins. Yield 19.3mg (79%). M.p. 225-226°C. Anal. Found: C, 39.12; H, 3.49 N, 14.26. Calc. for $C_{16}H_{14}N_5O_5Ag.1½H_2O$: C, 39.32; H, 3.69; N, 14.25. Crystals suitable for X-ray diffraction were obtained from vapour diffusion of diethyl ether into a nitromethane solution of **3.15**.

With palladium chloride, *viz* **3.17**.

Reaction of **3.13** with Li_2PdCl_4 in methanol gave a black precipitate that could not be identified.

With copper(II) chloride, *viz* **3.19**

Reaction of **3.13** (14.7mg, 0.05mmol) dissolved in hot methanol with copper (II) chloride (24.5mg, 0.10mmol) dissolved in hot methanol gave a green solution. A crystalline product appeared on standing overnight. Yield 18.4mg (93%). M.p. 236-237°C. Anal. Found: C, 38.59; H, 2.99; N, 11.02. Calc. for $C_{32}H_{28}N_8O_4Cu_3Cl_6$: C, 38.75; H, 2.85; N, 11.30.

With copper(I) iodide, *viz* **3.21**.

Reaction of **3.13** (14.6mg, 0.05mmol) dissolved in hot 1:1 acetone copper(I) iodide (19.4mg, 0.10mmol) dissolved in hot acetonitrile gave a yellow solution. A yellow solid appeared on standing. Yield 18.4mg (93%). M.p. >250°C. Anal. Found: C, 29.76; H, 1.97; N, 8.21. Calc. for $C_{16}H_{14}N_4O_2Cu_2I_2.¼(CH_3)_2CO$: C, 29.48; H, 2.26; N, 8.09.

With cadmium chloride, *viz* **3.23**

Reaction of **3.13** (14.6mg, 0.05mmol) dissolved in hot methanol with cadmium chloride (24.5mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing overnight. Yield 18.9mg (79%). M.p. 236-237°C. Anal. Found: C, 40.07; H, 2.85; N, 11.22. Calc. for $C_{16}H_{14}N_4O_2CdCl_2.¼MeOH$: C, 40.19; H, 3.11; N, 11.54. The complex was insoluble in common solvents.

6.4.4 Preparation of complexes with 3.14.

With silver nitrate, *viz* **3.16.**

Reaction of **3.14** (14.6mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.5mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A brown solid appeared on standing for 15 mins. Yield 19.3mg (79%). M.p. 225-226°C. Anal. Found: C, 50.85; H, 2.92; N, 12.10. Calc. for $C_{24}H_{18}N_5O_5Ag$: C, 51.08; H, 2.92; N, 12.10.

With palladium chloride, *viz* **3.18.**

Reaction of **3.14** (19.7mg, 0.05mmol) dissolved in hot acetone with a methanolic solution 0.151M of Li_2PdCl_4 (0.7mls, 0.11mmol) gave a yellow precipitate immediately. Yield 22.9mg (53%). M.p. >300°C (dec.). Anal. Found: C, 41.85; H, 3.46; N, 6.14. Calc. for $C_{24}H_{18}N_4O_2Pd_2Cl_4.3(CH_3)_2CO$: C, 41.64; H, 3.46; N, 6.10. The complex was insoluble in common solvents.

With copper(II) chloride, *viz* **3.20**

Reaction of **3.14** (19.7mg, 0.05mmol) dissolved in hot methanol with copper(II) chloride (24.6mg, 0.10mmol) dissolved in hot methanol gave a green solution. A green crystalline product appeared on standing overnight. Yield 18.4mg (93%). M.p. 281-284°C. Anal. Found: C, 42.31; H, 3.01; N, 8.45. Calc. for $C_{24}H_{18}N_4O_2Cu_2Cl_4.½H_2O$: C, 42.57; H, 2.85; N, 8.33.

With copper(I) iodide, *viz* **3.22**

Reaction of **3.14** (19.5mg, 0.05mmol) dissolved in hot 1:1 acetone-acetonitrile with copper(I) iodide (19.3mg, 0.10mmol) dissolved in hot acetonitrile gave a yellow solution. A yellow precipitate appeared on standing overnight. Yield 30.1mg (79%). M.p. >250°C (dec.). Anal. Found: C, 38.59; H, 2.75; N, 7.64. Calc. for $C_{24}H_{18}N_4O_2Cu_2I_2.½(CH_3)_2CO.CH_3CN$: C, 38.72; H, 2.48; N, 7.23.

With cadmium chloride, *viz* **3.24**

Reaction of **3.14** (14.6mg, 0.05mmol) dissolved in hot methanol with cadmium chloride (24.5mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline

product appeared on standing overnight. Yield 18.9mg (79%). M.p. 236-237°C. Anal. Found: C, 49.44; H, 2.90; N, 9.34. Calc. for $C_{24}H_{18}N_4O_2CdCl_2.½H_2O$: C, 49.13; H, 3.26; N, 9.55. The complex was insoluble in common solvents.

6.4.5 Preparation of complexes with 3.25.

With silver nitrate, *viz* **3.27.**

Reaction of **3.25** (14.6mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.0mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing for 30 mins. Yield 15.0mg (64%). M.p. 224-228°C. Anal. Found: C, 45.87; H, 3.67; N, 8.85. Calc. for $C_{18}H_{16}N_3O_5Ag.½H_2O$: C, 45.88; H, 3.64; N, 8.92. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of **3.27**.

With palladium chloride, *viz* **3.28.**

Reaction of **3.25** (14.7mg, 0.05mmol) dissolved in hot methanol with a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow solid immediately. Yield 23.9 mg (95%). M.p. >260°C (dec.). Anal. Found: C, 43.32; H, 3.62; N, 5.57. Calc. for $C_{18}H_{16}N_2O_2PdCl_2.1½H_2O$: C, 43.53; H, 3.86; N, 5.64. Insoluble in common NMR solvents.

With copper(II) nitrate, *viz* **3.29**

Reaction of **3.25** (14.7mg, 0.05mmol) dissolved in hot methanol with copper(II) nitrate (24.5mg, 0.10mmol) dissolved in hot methanol gave a blue solution. A crystalline product appeared on standing overnight. Yield 18.4mg (93%). M.p. 236-237°C. Anal. Found: C, 54.85; H, 4.22; N, 10.72. Calc. for $C_{36}H_{34}N_6O_{10}Cu.H_2O$: C, 54.72; H, 4.34; N, 10.63. Single crystals were obtained from a methanol solution of copper nitrate layered onto a dichloromethane solution of **3.25**.

With copper(I) iodide, *viz* **3.30.**

A solution of copper(I) iodide (19.5mg, 0.10mmol) in acetonitrile (10mls) was carefully

layered onto a solution of **3.25** (14.6mg, 0.05mmol) dissolved in dichloromethane (10mls). A crystalline product appeared on standing overnight. Yield 28.6mg (85%). M.p. 298-299°C . Anal. Found: C, 32.26; H, 2.19 N, 4.12. Calc. for $C_{18}H_{16}N_2O_2Cu_2I_2$: C, 32.11 H, 2.40; N, 4.16.

With copper(I) bistriphenylphosphine nitrate, *viz* **3.31**

Reaction of **3.25** (14.7mg, 0.05mmol) dissolved in hot methanol with copper(I) bistriphenylphosphine nitrate (65.4mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. Large colourless crystals, suitable for X-ray structure analysis, formed on standing overnight. Yield 55.6mg (69%). M.p. 144-146°C. Anal. Found: C, 67.95; H, 5.00; N, 3.87. Calc. for $C_{90}H_{76}N_4O_8P_4Cu_2$: C, 67.88; H, 4.81; N, 3.52.

With cadmium nitrate, *viz* **3.32.**

Reaction of **3.25** (14.6mg, 0.05mmol) dissolved in hot methanol with cadmium nitrate (31.4mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing for 1 hr. Yield 13.7mg (66%). M.p. >250°C (dec.). Anal. Found: C, 52.53; H, 3.72; N, 10.26. Calc. for $C_{36}H_{32}N_6O_{10}Cd.H_2O$: C, 52.66; H, 3.93; N, 10.24. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother liquor after filtration.

With zinc bromide, *viz* **3.33.**

A solution of zinc bromide (14.7mg, 0.05mmol) in methanol (10mls) was carefully layered onto a solution of **3.25** (23.9mg, 0.11mmol) dissolved in dichloromethane (10mls). Single crystals suitable for X-ray structure analysis were isolated on standing. Yield 22.9mg (90%). M.p. >260°C (dec.). Anal. Found: C, 41.87; H, 2.99 N, 5.35. Calc. for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.77; H, 3.12; N, 5.41.

6.4.6 Preparation of complexes with 3.26.

With silver tetrafluoroborate, *viz* **3.34.**

Reaction of **3.26** (14.7mg, 0.05mmol) dissolved in hot acetonitrile with silver tetrafluoroborate (20.1mg, 0.10mmol) dissolved in hot acetonitrile gave a colourless

solution. A crystalline product formed upon diffusion of ether into the mother liquor. Yield 19.2mg (70%). M.p. 190-191°C. Anal. Found: C, 45.88; H, 3.73; N, 8.73. Calc. for $C_{18}H_{16}N_2O_2BF_4Ag.1½CH_3CN$: C, 45.98; H, 3.77; N, 8.94.

With palladium chloride, *viz* **3.35.**

Reaction of **3.26** (14.4mg, 0.05mmol) dissolved in hot methanol and a methanolic solution of 0.1511M Li_2PdCl_4 (0.7ml, 0.10mmol) gave a yellow solid immediately. Yield 15.6 mg (65%). M.p. >270°C (dec.). Anal. Found: C, 44.53; H, 3.52; N, 5.57. Calc. for $C_{18}H_{16}N_2O_2PdCl_2$: C, 44.33; H, 3.72; N, 5.74. Insoluble in common NMR solvents.

With copper(II) nitrate, *viz* **3.36.**

Reaction of **3.26** (14.5mg, 0.05mmol) with copper(II) nitrate in methanol gave a blue solution. A blue precipitate formed overnight. Yield 17.8mg (74%). M.p. 220°C (dec.). Anal. Found: C, 45.05; H, 3.36; N, 11.67. Calc. for $C_{18}H_{16}N_4O_8Cu$: C, 45.27; H, 3.33; N, 11.37. Crystals suitable for single crystal structural analysis were grown by layering a solution of copper(II) nitrate in methanol onto a dichloromethane solution of **3.26**.

With copper(I) iodide, *viz* **3.37.**

A solution of copper(I) iodide (19.5mg, 0.10mmol) in acetonitrile (10mls) was carefully layered onto a solution of **3.26** (14.6mg, 0.05mmol) dissolved in dichloromethane (10mls). A crystalline product appeared on standing overnight. Yield 22.6mg (69%). M.p. >250°C (dec.). Anal. Found: C, 32.59; H, 2.38 N, 4.19. Calc. for $C_{18}H_{16}N_2O_2Cu_2I_2.½CH_3CN$: C, 32.26 H, 2.58; N, 4.38.

With cadmium nitrate, *viz* **3.38.**

Reaction of **3.26** (14.4mg, 0.05mmol) dissolved in hot methanol with cadmium nitrate (31.1mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing for 1 hr. Yield 16.4mg (70%). M.p. 222-224°C (dec.). Anal. Found: C, 46.12; H, 3.95; N, 10.02. Calc. for $C_{72}H_{68}N_{14}O_{26}Cd_3$.MeOH: C, 45.98; H, 3.59; N, 10.26. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother liquor after filtration.

With zinc bromide, *viz* **3.39**.

A solution of zinc bromide (14.6mg, 0.05mmol) in methanol (10mls) was carefully layered onto a solution of **3.26** (23.9mg, 0.11mmol) dissolved in dichloromethane (10mls). A crystalline product appeared on standing overnight. Yield 21.6mg (84%). M.p. >270°C (dec.). Anal. Found: C, 41.63; H, 2.96 N, 5.26. Calc. for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.77 H, 3.12; N, 5.41.

6.4.7 Preparation of complexes with 3.40

With silver nitrate, *viz* **3.43**.

Reaction of **3.40** (14.6mg, 0.05mmol) in acetone with silver nitrate (17.3mg, 0.10mmol) in methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into the reaction mixture. Yield 12.1mg (52%). M.p. 134-135°C. Anal. Found: C, 46.39; H, 3.45; N, 8.79. Calc. for $C_{18}H_{16}N_3O_5Ag$: C, 46.77; H, 3.49; N, 9.09.

With copper(II) chloride, *viz* **3.44**.

Reaction of **3.40** (14.6mg, 0.05mmol) in methanol with copper(II) chloride (17.6mg, 0.10mmol) gave a green precipitate on standing overnight. Yield 14.3mg (67%). M.p. 137-138°. Anal. Found: C, 50.66; H, 3.78; N, 6.56. Calc. for $C_{18}H_{16}N_2O_2CuCl_2$: C, 50.70; H, 3.67; N, 6.50. Crystals suitable for X-Ray structure analysis were obtained by layering a solution of copper(II) chloride onto a dichloromethane solution of **3.40**.

With cadmium nitrate, *viz* **3.45**.

Reaction of **3.40** (14.4mg, 0.05mmol) in methanol with cadmium nitrate (33.4mg 0.11mmol) in methanol gave a white precipitate immediately. This precipitate was filtered off and washed (1x2mls MeOH). Yield 21.5mg (83%). M.p. >250° (dec.). Anal. Found: C, 41.07; H, 2.98; N, 10.54. Calc. for $C_{18}H_{16}N_4O_8Cd$: C, 40.89; H, 3.05; N, 10.60.

With zinc bromide, *viz* **3.46**.

Reaction of **3.40** (14.7mg, 0.05mmol) in methanol with zinc bromide (24.1mg, 0.11mmol)

in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 19.6mg (75%) M.p. >250° (dec.). Anal Found: C, 41.55; H, 3.06; N, 5.20. Calc for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.77; H, 3.12; N, 5.41.

6.4.8 Preparation of complexes with 3.41

With silver nitrate, *viz* **3.47**.

Reaction of **3.41** (14.6mg, 0.05mmol) in acetone with silver nitrate (17.4mg, 0.10mmol) in methanol gave a colourless solution. A crystalline product appeared on standing for overnight. Yield 22.9mg (79%). M.p. 197-199°C. Anal. Found: C, 40.70; H, 3.39; N, 8.78. Calc. for $C_{36}H_{32}N_7O_{13}Ag_3.(CH_3)_2CO$: C, 40.65; H, 3.32; N, 8.51. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into an acetonitrile solution of **3.41**.

With copper(II) chloride, *viz* **3.48**.

Reaction of **3.41** (14.4mg, 0.05mmol) in methanol with copper(II) chloride (17.6mg, 0.10mmol) gave a blue precipitate on standing overnight. Yield 14.3mg (67%). M.p. >250° (dec.). Anal. Found: C, 49.83; H, 3.89; N, 6.34. Calc. for $C_{18}H_{16}N_2O_2CuCl_2.½MeOH$: C, 50.18; H, 4.25; N, 6.33.

With cadmium nitrate, *viz* **3.49**

Reaction of **3.41** (14.3mg, 0.05mmol) in methanol with cadmium nitrate (31.7mg 0.11mmol) in methanol gave a colourless solution. Crystals suitable for X-ray structure analysis were obtained by slow evaporation of this solution. Yield 15.1mg (74%) M.p. 251-253°C. Anal. Found: C, 51.84; H, 4.31; N, 10.44. Calc. for $C_{36}H_{32}N_6O_8Cd.2½H_2O$: C, 51.81; H, 4.31; N, 10.08.

With zinc bromide, *viz* **3.50**

Reaction of **3.41** (14.6mg, 0.05mmol) in methanol with zinc bromide (22.9mg, 0.10mmol) in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 18.9mg (73%) M.p. 221-223°. Anal Found: C, 41.48; H, 3.12; N, 5.14. Calc for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.77; H, 3.12; N, 5.41. Single crystals

suitable for X-ray structure analysis were grown by layering a methanol solution of zinc bromide onto a dichloromethane solution of **3.41**.

6.4.9 Preparation of complexes with 3.42

With silver nitrate, *viz* **3.51**.

Reaction of **3.42** (14.4mg, 0.05mmol) in acetone with silver nitrate (17.4mg, 0.10mmol) in methanol gave a light brown precipitate immediately. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into an acetonitrile solution of **3.42**. Yield 19.2mg (84%). M.p. 164-165°C. Anal. Found: C, 46.76; H, 3.49; N, 9.09. Calc. for $C_{18}H_{16}N_3O_5Ag$: C, 46.80; H, 3.50; N, 9.09.

With copper(II) nitrate, *viz* **3.52**.

Reaction of **3.42** (14.6mg, 0.05mmol) dissolved in hot methanol with copper(II) nitrate (26.2mg, 0.11mmol) dissolved in hot methanol gave a blue solution. Small blue crystals were obtained on standing for 3 days. Yield 17.1mg (85%). M.p. >300°C (dec.). Anal. Found: C, 53.21; H, 4.21; N, 10.19. Calc. for $C_{36}H_{32}N_6O_{10}Cu.2H_2O$: C, 53.50; H, 4.49; N, 10.40.

With cadmium nitrate, *viz* **3.53**.

Reaction of **3.43** (14.7mg, 0.05mmol) in methanol with cadmium nitrate (32.2mg 0.11mmol) in methanol gave a white precipitate immediately. This precipitate was filtered off and washed (2x2mls MeOH). Yield 18.1mg (68%). M.p. >300°(dec.). Anal. Found: C, 40.87; H, 2.95; N, 10.54. Calc. for $C_{18}H_{16}N_4O_8Cd$: C, 40.89; H, 3.05; N, 10.60.

With zinc bromide, *viz* **3.54**.

Reaction of **3.43** (14.4mg, 0.05mmol) in methanol with zinc bromide (23.7mg, 0.10mmol) in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 19.4mg (75%) M.p. >250° (dec.). Anal Found: C, 40.96; H, 2.99; N, 5.14. Calc for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.06; H, 3.25; N, 5.32.

6.4.10 Preparation of complexes with 3.55

With silver nitrate, *viz* **3.58.**

Reaction of **3.55** (14.7mg, 0.05mmol) in acetone with silver nitrate (17.5mg, 0.10mmol) in methanol gave crystals suitable for X-ray diffraction on standing overnight. Yield 18.5mg (81%). M.p. 199-200°C. Anal. Found: C, 46.69; H, 3.54; N, 9.09. Calc. for $C_{18}H_{16}N_3O_5Ag$: C, 46.80; H, 3.50; N, 9.09.

With copper(II) chloride, *viz* **3.59.**

Reaction of **3.55** (14.4mg, 0.05mmol) in methanol with copper(II) chloride (17.6mg, 0.10mmol) gave a blue precipitate on standing overnight. Yield 14.3mg (67%). M.p. >250° (dec.). Anal. Found: C, 50.22; H, 4.25; N, 6.33. Calc. for $C_{18}H_{16}N_2O_2CuCl_2.½MeOH$: C, 50.18; H, 4.25; N, 6.33.

With cadmium nitrate, *viz* **3.60.**

Reaction of **3.55** (14.7mg, 0.05mmol) in methanol with cadmium nitrate (32.2mg 0.11mmol) in methanol gave a white precipitate immediately. This precipitate was filtered off and washed (2x2mls MeOH). Yield 20.1mg (77%). M.p. >300° (dec.). Anal. Found: C, 41.03; H, 2.86; N, 10.47. Calc. for $C_{18}H_{16}N_4O_8Cd$: C, 40.89; H, 3.05; N, 10.60.

With zinc bromide, *viz* **3.61.**

Reaction of **3.55** (14.6mg, 0.05mmol) in methanol with zinc bromide (24.1mg, 0.11mmol) in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 19.4mg (67%) M.p. >300°(dec.). Anal Found: C, 43.42; H, 3.73; N, 5.13. Calc for $C_{18}H_{16}N_2O_2ZnBr_2.(CH_3)_2CO$: C, 43.82; H, 3.73; N, 4.87. Single crystals suitable for X-ray structure analysis were grown by layering a methanol solution of zinc bromide onto a dichloromethane solution of **3.55**.

6.4.11 Preparation of complexes with 3.56

With silver nitrate, *viz* **3.62.**

Reaction of **3.56** (14.6mg, 0.05mmol) in acetone with silver nitrate (17.2mg, 0.10mmol) in

methanol gave small needle-like crystals after standing for one hour. Yield 19.2mg (84%). M.p. 179-181°C. Anal. Found: C, 42.45; H, 3.12; N, 8.70. Calc. for $C_{54}H_{48}N_{10}O_{18}Ag_4.½(CH_3)_2CO$: C, 42.75; H, 3.50; N, 8.52. Crystals suitable for X-ray diffraction were obtained by diffusion of ether into an acetonitrile solution of **3.62**.

With copper(II) nitrate, *viz* **3.63**.

Reaction of **3.56** (14.6mg, 0.05mmol) dissolved in hot methanol with copper(II) nitrate (26.2mg, 0.11mmol) dissolved in hot methanol gave a blue solution. A blue crystalline complex formed over 24 hours. Yield 19.7mg (81%). M.p. >270°C (dec.). Anal. Found: C, 44.52; H, 3.30; N, 11.41. Calc. for $C_{18}H_{16}N_4O_8Cu.½H_2O$: C, 44.22; H, 3.50; N, 11.41.

With cadmium nitrate, *viz* **3.64**.

Reaction of **3.56** (14.4mg, 0.05mmol) in methanol with cadmium nitrate (32.2mg 0.11mmol) in methanol gave a colourless solution. A colourless crystalline precipitate was isolated by diffusion of ether into the reaction mixture. Yield 14.1mg (54%). M.p. 191-193°C. Anal. Found: C, 41.24; H, 2.90; N, 10.29. Calc. for $C_{18}H_{16}N_4O_8Cd$: C, 40.89; H, 3.05; N, 10.60.

With zinc bromide, *viz* **3.65**.

Reaction of **3.56** (14.6mg, 0.05mmol) in methanol with zinc bromide (23.5mg, 0.11mmol) in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 20.0mg (77%) M.p. 202-204°C. Anal Found: C, 41.61; H, 3.16; N, 5.33. Calc for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.77; H, 3.12; N, 5.41.

6.4.12 Preparation of complexes with 3.57

With silver nitrate, *viz* **3.66**.

Reaction of **3.57** (14.4mg, 0.05mmol) in acetone with silver nitrate (17.4mg, 0.10mmol) in methanol gave a light brown precipitate immediately. Yield 19.1mg (84%). M.p. >200°C (dec.). Anal. Found: C, 46.40; H, 3.39; N, 8.92. Calc. for $C_{18}H_{16}N_3O_5Ag$: C, 46.80; H, 3.50; N, 9.09.

With copper(II) chloride, *viz* **3.67.**

Reaction of **3.57** (14.4mg, 0.05mmol) in methanol with copper(II) chloride (17.6mg, 0.10mmol) gave a blue precipitate on standing overnight. Yield 15.1mg (71%). M.p. >280° (dec.). Anal. Found: C, 50.61; H, 3.76; N, 6.47. Calc. for $C_{18}H_{16}N_2O_2CuCl_2$: C, 50.66; H, 3.78; N, 6.56.

With cadmium nitrate, *viz* **3.68.**

Reaction of **3.57** (14.6mg, 0.05mmol) in methanol with cadmium nitrate (31.9mg 0.11mmol) in methanol gave a colourless solution. Crystals suitable for X-ray structure analysis were obtained by slow evaporation of this solution. Yield 15.1mg (74%) M.p. 150°C (dec.). Anal. Found: C, 51.15; H, 4.21; N, 9.69. Calc. for $C_{36}H_{32}N_6O_{10}Cd.H_2O$: C, 51.33; H, 4.08; N, 10.60.

With zinc bromide, *viz* **3.69.**

Reaction of **3.57** (14.6mg, 0.05mmol) in methanol with zinc bromide (23.5mg, 0.11mmol) in methanol gave a colourless solution. A colourless crystalline product appeared on standing at R.T. overnight. Yield 16.5mg (64%) M.p. >250°C (dec.). Anal Found: C, 41.77; H, 3.12; N, 5.41. Calc for $C_{18}H_{16}N_2O_2ZnBr_2$: C, 41.47; H, 3.20; N, 5.41.

6.4.13 Preparation of complexes with 3.70.

With silver nitrate, *viz* **3.73.**

Reaction of **3.70** (19.8mg, 0.05mmol) in methanol with silver nitrate (26.2mg, 0.16mmol) in methanol gave a colourless solution. A crystalline product appeared on standing for 30 mins. Yield 36.0mg (98%). M.p. 199-200°C. Anal. Found: C, 39.07; H, 2.76; N, 9.35. Calc. for $C_{24}H_{21}N_5O_9Ag_2$: C, 39.00; H, 2.86; N, 9.47. Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into an acetonitrile solution of **3.73.**

With copper(II) chloride, *viz* **3.74.**

A solution of copper(II) chloride (26.0mg, 0.15mmol) in methanol (10mls) was carefully layered onto a solution of **3.70** (19.8mg, 0.05mmol) dissolved in dichloromethane (10mls).

Large green crystals appeared on standing overnight. Yield 26.1mg (63%). M.p. 148-150 °C. Anal. Found: C, 44.66; H, 3.73; N, 6.50 ; Calc. for $C_{48}H_{42}N_6O_6Cu_3Cl_6$: C, 44.92; H, 4.01; N, 6.55.

With cadmium nitrate, *viz* **3.75.**

Reaction of **3.70** (14.6mg, 0.05mmol) in methanol with cadmium nitrate (31.9mg, 0.11mmol) in methanol gave a colourless solution. The solution was reduced to 2mls *in vacuo*. A crystalline powder was isolated by diffusion of ether into the solution. Yield 19.9mg (52%). M.p. >250°C (dec.). Anal. Found: C, 26.19; H, 1.34; N, 11.51. Calc for $C_{24}H_{18}N_9O_{21}Cd$: C, 26.07; H, 1.64; N, 11.40.

With zinc bromide, *viz* **3.76.**

A solution of zinc bromide (37.5mg 0.16mmol) in methanol (10mls) was carefully layered onto a solution of **3.70** (19.9mg, 0.05mmol) dissolved in dichloromethane (10mls). A crystalline product appeared on standing overnight. Yield 29.1mg (81%). M.p. 206-207 (dec.) °C. Anal. Found: C, 46.15; H, 3.39; N, 6.73; Calc. for $C_{24}H_{21}N_3O_2ZnBr_2$: C, 45.92; H, 3.41; N, 6.62.

6.4.14 Preparation of complexes with 3.71.

With silver tetrafluoroborate, *viz* **3.77.**

Reaction of **3.71** (20.0mg, 0.05mmol) in acetonitrile with silver tetrafluoroborate (31.2mg, 0.16mmol) in acetonitrile gave a colourless solution. Crystals suitable for Xray crystallography were obtained from diffusion of pentane into this solution. Yield 25.4mg (73%). M.p. > 260°C (dec.). Anal. Found: C, 41.51; H, 3.41; N, 5.88. Calc. for $C_{48}H_{42}N_6O_6Ag_3B_3F_{12}$: C, 41.72; H, 3.06; N, 6.08.

With copper(II) nitrate, *viz* **3.78**

Reaction of **3.71** (19.9mg, 0.05mmol) dissolved in hot methanol with copper(II) nitrate (36.9mg, 0.15mmol) dissolved in hot methanol gave a blue solution. A blue precipitate appeared after 5mins. Yield 29.6mg (97%). M.p. 212-214°C. Anal. Found: C, 46.81; H, 3.78; N, 11.42. Calc. for $C_{24}H_{21}N_5O_9Cu.1½H_2O$: C, 46.95; H, 3.94; N, 11.41.

With cadmium nitrate, *viz* **3.79.**

Reaction of **3.71** (20.0mg, 0.05mmol) dissolved in hot methanol with cadmium nitrate (47.0mg, 0.15mmol) dissolved in hot methanol gave a colourless solution. Small crystals appeared on standing overnight. Yield 29.3mg (90%). M.p. 193-194°C (dec.). Anal. Found: C, 44.08; H, 3.55; N, 10.71. Calc. for $C_{24}H_{21}N_5O_9Cd.H_2O$: C, 44.31; H, 3.55; N, 10.71.

With zinc bromide, *viz* **3.80.**

Reaction of **3.71** (19.7mg, 0.05mmol) dissolved in hot methanol with zinc bromide (35.7mg, 0.16mmol) dissolved in hot methanol gave a white precipitate immediately. Yield 26.7mg (73%). M.p. 267-268°C. Anal. Found: C, 39.27; H, 2.81; N, 5.51. Calc. for $C_{48}H_{42}N_6O_6Zn_3Br_6$: C, 39.10; H, 2.87; N, 5.70.

6.4.15 Preparation of complexes with 3.72.

With silver tetrafluoroborate, *viz* **3.81.**

Reaction of **3.72** (19.8mg, 0.05mmol) in acetonitrile with silver tetrafluoroborate (32.1mg, 0.16mmol) in acetonitrile gave a colourless solution. A fawn precipitate appeared on standing overnight. Yield 28.7mg (95%). M.p. 185-187°C (dec.). Anal. Found: C, 46.84; H, 3.52; N, 6.75. Calc. for $C_{24}H_{21}N_3O_3AgBF_4.H_2O$: C, 47.09; H, 3.79; N, 6.86.

With copper(II) nitrate, *viz* **3.82**

Reaction of **3.72** (20.1mg, 0.05mmol) dissolved in hot methanol with copper(II) nitrate (37.1mg, 0.15mmol) dissolved in hot methanol gave a blue precipitate immediately. Yield 26.5mg (85%). M.p. >250°C (dec.). Anal. Found: C, 46.68; H, 3.78; N, 11.50. Calc. for $C_{24}H_{21}N_5O_9Cu.1\frac{1}{2}H_2O$: C, 46.95; H, 3.94; N, 11.41.

With cadmium nitrate, *viz* **3.83.**

Reaction of **3.72** (20.0mg, 0.05mmol) dissolved in hot methanol with cadmium nitrate (47.1mg, 0.15mmol) dissolved in hot methanol gave a colourless solution. Large crystals appeared on standing for five days. Yield 23.1mg (68%). M.p. >300°C (dec.). Anal.

Found: C, 43.23; H, 3.11; N, 10.25. Calc. for $C_{24}H_{21}N_5O_9Cd.½CH_2Cl_2$: C, 43.41; H, 3.20; N, 10.33.

With zinc bromide, *viz* **3.84.**

Reaction of **3.72** (20.0mg, 0.05mmol) dissolved in hot methanol with zinc bromide (35.5mg, 0.16mmol) dissolved in hot methanol gave a white precipitate immediately. Yield 25.1mg (76%). M.p. > 220°C (dec.). Anal. Found: C, 45.64; H, 3.31; N, 6.63. Calc. for $C_{24}H_{21}N_3O_3ZnBr_2.½H_2O$: C, 45.49; H, 3.31; N, 6.63.

6.5 Chiral Coordination Polymer Complexes

6.5.1 Preparation of complexes with 4.1.

With silver nitrate, *viz* **4.3.**

Reaction of **4.1** (19.0mg, 0.1mmol) dissolved in hot acetone with silver nitrate (17.8mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A crystalline product appeared on standing for 30 mins. Yield 26.4mg (73%). M.p. 274-275°C. Anal. Found: C, 40.24; H, 4.32; N, 11.89. Calc. for $C_{12}H_{16}N_3O_3Ag$: C, 40.24; H, 4.50; N, 11.73. Crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile solution of **4.3**.

With copper(II) nitrate, *viz* **4.4.**

Reaction of **4.1** (9.6mg, 0.051mmol) dissolved in hot methanol with copper(II) nitrate (24.8mg, 0.10mmol) dissolved in hot methanol gave a blue solution. A crystalline product suitable for X-ray crystal structure analysis appeared on evaporation of the reaction mixture. Yield 12.2mg (80%). M.p. >200°C (dec.). Anal. Found: C, 31.24; H, 4.28; N, 13.26. Calc. for $C_{36}H_{48}N_{14}O_{24}Cu_4.4H_2O.2MeOH$: C, 31.45; H, 4.45; N, 13.51.

With copper(I) iodide, *viz* **4.5.**

Reaction of **4.1** (18.7mg, 0.1mmol) dissolved in acetonitrile with copper(I) iodide (19.3mg, 0.10mmol) dissolved in hot acetonitrile gave a yellow solution. Crystals suitable

for X-ray diffraction were obtained by slow evaporation of the reaction mixture. Yield 21.6mg (73%). M.p. 208-209°C. Anal. Found: C, 38.09; H, 4.29; N, 7.39. Calc. for $C_{12}H_{16}N_2CuI$: C, 38.06; H, 4.26; N, 7.40. ^{1}H NMR (300MHz, CD_3CN): δ 8.35 (1H, m, H8,H9), 3.36 (1H, d, H4), 2.28 (1H, m, $H6_{exo}$), 2.05 (1H, m, $H5_{exo}$), 1.36 (3H, s, H1-Me), 1.27 (2H, dd, $H5_{endo}$, $H6_{endo}$), 1.11 (3H, s, H7-*anti*), 0.60 (3H, s, H7-*syn*).

With zinc bromide, *viz* **4.6.**

Reaction of **4.1** (9.3mg, 0.05mmol) dissolved in methanol with zinc bromide (23.4mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained by slow evaporation the reaction mixture. Yield 15.6mg (64%). M.p. 223-224°C. Anal. Found: C, 46.68; H, 5.38 N, 9.05. Calc. for $C_{24}H_{36}N_2ZnBr_2.H_2O$: C, 46.59; H, 5.21; N, 9.07.

6.5.2 Preparation of complexes with 4.7.

With silver nitrate, *viz* **4.9.**

Reaction of **4.7** (14.9mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.4mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained on cooling. An analytically pure sample was obtained by addition of ether to the solution. Yield 7.5mg (31%). M.p. >265°C (dec.). Anal. Found: C, 50.16; H, 5.99; N, 8.55. Calc. for $C_{40}H_{56}N_6O_6Ag_2.MeOH.H_2O$: C, 50.11; H, 6.36; N, 8.55.

With copper(I) iodide, *viz* **4.10.**

Reaction of **4.7** (14.7mg, 0.05mmol) in hot acetonitrile with copper(I) iodide (9.8mg, 0.051mmol) in hot acetonitrile gave a yellow solution. Yellow crystals suitable for single crystal X-ray structure determination were obtained from the slow evaporation of this solution. Yield 15.7mg (76%). M.p. >310°C (dec.). Anal. Found: C, 43.57; H, 4.84; N, 5.20. Calc. for $C_{30}H_{42}N_3Cu_2I_2$: C, 43.65; H, 5.13; N, 5.09. ^{1}H NMR (300MHz, CD_3CN): δ 2.92 (2H, d, H4), 2.28 (2H, m, $H6_{exo}$), 2.04 (2H, m, $H5_{exo}$), 1.37 (6H, s, H1-Me), 1.22 (4H, dd, $H5_{endo}$, $H6_{endo}$), 1.10 (6H, s, H7-*anti*), 0.66 (6H, s, H7-*syn*).

6.5.3 Preparation of complexes with 4.8.

With silver nitrate, *viz* **4.11.**

Reaction of **4.8** (14.6mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.3mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained on cooling. Yield 8.9mg (30%). M.p. >250°C (dec.). Anal. Found: C, 49.60; H, 6.24; N, 8.68. Calc. for $C_{20}H_{28}N_3O_3Ag.H_2O$: C, 50.00; H, 6.40; N, 8.29.

6.5.4 Preparation of complexes with 4.12.

With silver nitrate, *viz* **4.14,**

Reaction of **4.12** (19.9mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.5mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. Crystals suitable for X-ray diffraction were obtained on standing. Yield 18.9mg (51%). M.p. >200°C (dec.). Anal. Found: C, 41.98; H, 4.19; N, 11.28. Calc. for $C_{26}H_{30}N_6O_6Ag_2$: C, 42.30; H, 4.10; N, 11.38.

6.5.5 Preparation of complexes with 4.13.

With silver nitrate, *viz* **4.15.**

Reaction of **3.13** (20.0mg, 0.05mmol) dissolved in hot acetone with silver nitrate (17.2mg, 0.10mmol) dissolved in hot methanol gave a colourless solution. A colourless precipitate appeared after standing for 5 mins. Yield 21.5mg (58%). M.p. >250°C (dec.). Anal. Found: C, 41.51; H, 4.22; N, 11.19. Calc. for $C_{26}H_{30}N_6O_6Ag_2.H_2O$: C, 41.29; H, 4.26; N, 11.11.

Crystallography

Crystallography

Tables **C1 – C10** list crystal data and X-ray experimental details for the forty nine crystal structures discussed in this thesis. Selected bond lengths and angles are listed in the discussion of the structures, and the remaining distances and angles, as well as atom coordinates, anisotropic displacement parameters and hydrogen atom coordinates are available from the Chemistry Department, University of Canterbury.

All measurements were made with a Siemens CCD area detector using graphite monochromised Mo Kα (λ = 0.71073 Å) radiation at the temperature indicated in the following tables. The data reduction was performed using SAINT.[221] Intensities were corrected for Lorentz and polarisation effects and for absorption using SADABS.[222] Space groups were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using SHELXS,[223] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[224] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. Absolute structure determinations were based on the Flack parameter. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [\max(F_o)^2 + 2F_c^2]/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

Table C1 – Crystal data and X-ray experimental details for **2.1**, **2.4**, **2.3**, **2.2** and **2.7**.

Compound		**2.1**	**2.4**	**2.3**	**2.2**	**2.7**
Empirical formula		$C_{16}H_{10}N_4$	$C_{18}H_{12}N_2$	$C_{16}H_{10}N_4$	$C_{16}H_{10}N_4$	$C_{16}H_{10}C_{12}N_4Pd$
Formula weight		258.28	128.15	258.28	258.28	435.58
Temperature (K)		170(2)	163(2)	163(2)	163(2)	163(2)
Crystal system		Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorombic
Space group		$P2_1/n$	$P2_1/n$	$P2_1/n$	C2	Pbcn
Unit cell dimensions:	a (Å)	8.557(4)	8.964(6)	5.779(3)	22.523(17)	10.253(3)
	b (Å)	6.330(3)	6.265(4)	5.350(3)	3.912(3)	20.818(7)
	c (Å)	11.841(5)	11.241(8)	18.906(10)	6.979(5)	7.096(2)
	α (°)	90	90	90	90	90
	β (°)	106.689(6)	107.109(18)	91.466(7)	106.140(10)	90
	γ (°)	90	90	90	90	90
Volume($Å^3$)		614.4(5)	603.3(7)	584.3(5)	590.6(7)	1514.6(9)
Z		2	2	2	2	4
Density (calculated) (Mg/m^3)		1.396	1.411	1.468	1.452	1.910
Absorption coefficient (mm^{-1})		0.087	0.084	0.092	0.091	1.581
F(000)		268	268	268	268	856
Crystal size (mm)		0.75 x 0.25 x 0.12	0.35 x 0.25 x 0.01	0.30 x 0.30 x 0.15	0.59 x 0.20 x 0.05	0.62 x 0.24 x 0.01
Theta range for data collection (°)		2.61 to 26.46	2.57 to 26.43	2.16 to 26.36	3.04 to 25.20	2.21 to 26.37
Reflections collected		7439	7524	6979	3477	13169
Independent reflections [R(int)]		1253 [0.0300]	1237 [0.0767]	1190 [0.0133]	967 [0.0334]	1535 [0.0399]
Observed reflections [$I>2\sigma(I)$]		891	562	954	792	1106
Data / restraints / parameters		1253 / 0 / 91	1237 / 0 / 92	1190 / 0 / 91	967 / 1 / 92	1535 / 0 / 105
Goodness-of-fit on F^2		1.026	0.796	1.064	1.022	1.017
R_1 [I>2sigma(I)]		0.0547	0.0451	0.0359	0.0478	0.0228
wR_2 (all data)		0.1328	0.1092	0.1112	0.1238	0.0603

Table C2 – Crystal data and X-ray experimental details for **2.8**, **2.10**, **2.14**, **2.16** and **2.17**.

Compound		**2.8**	**2.10**	**2.14**	**2.16**	**2.17**
Empirical formula		$C_{18.75}H_{13}Cl_2N_{4.81}O_{1.5}Cu$	$C_{17}H_{16}N_6O_8Cd$	$C_{16}H_{10}N_5O_3Ag$	$C_{17}H_{14}N_4OCl_2Cu$	$C_{16}H_{10}N_4CuI$
Formula weight		464.15	544.76	428.16	424.76	448.72
Temperature (K)		168(2)	173(2)	163(2)	163(2)	163(2)
Crystal system		Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group		C2/c	$P2_1/n$	$P2_1/n$	$P2_1/c$	P-1
Unit cell dimensions:	a (Å)	17.248(8)	7.313(2)	5.204(2)	6.422(3)	8.803(3)
	b (Å)	11.026(5)	19.961(7)	18.144(8)	17.547(9)	9.075(3)
	c (Å)	21.533(10)	13.306(4)	16.841(7)	15.140(8)	10.273(3)
	α (°)	90	90	90	90	88.022(4)
	β (°)	112.869(6)	97.533(5)	98.400(5)	100.063(7)	65.351(4)
	γ (°)	90	90	90	90	79.028(4)
Volume($Å^3$)		3773(3)	1925.6(11)	1573.0(12)	1679.8(15)	731.4(4)
Z		8	4	4	4	2
Density (calculated) (Mg/m^3)		1.634	1.879	1.808	1.680	2.038
Absorption coefficient (mm^{-1})		1.464	1.197	1.309	1.631	3.604
F(000)		1874	1088	848	860	432
Crystal size (mm^3)		0.34 x 0.19 x 0.02	0.47 x 0.15 x 0.08	0.50 x 0.14 x 0.10	0.27 x 0.10 x 0.03	0.35 x 0.20 x 0.03
Theta range for data collection (°)		2.05 to 26.37	1.85 to 26.41	2.24 to 26.41	2.32 to 26.40	2.18 to 26.34
Reflections collected		23865	24163	19251	21107	9107
Independent reflections [R(int)]		3843 [0.0679]	3926 [0.0304]	3179 [0.0385]	3411 [0.0676]	2888 [0.0188]
Observed reflections [$I>2\sigma(I)$]		2549	3436	2433	2039	2550
Data / restraints / parameters		3843 / 0 / 280	3926 / 0 / 298	3179 / 0 / 226	3411 / 0 / 229	2888 / 0 / 199
Goodness-of-fit on F^2		0.927	1.011	0.959	0.922	0.981
R_1 [I>2sigma(I)]		0.0373	0.0209	0.0298	0.0367	0.0234
wR_2 (all data)		0.0919	0.0503	0.0742	0.0966	0.0578

Table C3 – Crystal data and X-ray experimental details for **2.19**, **2.25**, **2.27**, **3.9** and **3.10**.

Compound		**2.19**	**2.25**	**2.27**	**3.9**	**3.10**
Empirical formula		$C_{52}H_{40}CuN_5O_3P_2$	$C_{26}H_{18}B_2F_8N_7Ag_2$	$C_{18}H_{13}N_7O_6Cu$	$C_{14}H_{10}N_4O_2Cu_2I_2$	$C_{22}H_1N_4O_{24}Cu_2I_2$
Formula weight		908.37	817.83	486.89	647.14	747.25
Temperature (K)		203(2)	168(2)	168(2)	163(2)	163(2)
Crystal system		Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group		P-1	P-1	P-1	P-1	$P2_1/n$
Unit cell dimensions:	a (Å)	12.753(7)	10.639(4)	8.889(4)	4.2519(15)	4.264(4)
	b (Å)	14.889(8)	10.704(4)	9.778(4)	7.880(3)	17.618(15)
	c (Å)	15.340(8)	12.821(5)	13.041(5)	12.934(5)	13.977(12)
	α (°)	69.043(7)	83.767(5)	102.165(5)	74.427(5)	90
	β (°)	88.944(7)	67.201(5)	97.835(5)	83.583(4)	97.414(12)
	γ (°)	65.952(8)	83.379(5)	114.229(5)	79.881(4)	90
Volume($Å^3$)		2456(2)	1333(1)	978.3(7)	410.0(2)	1041.2(15)
Z		2	2	2	1	2
Density (calculated) (Mg/m^3)		1.228	2.036	1.653	2.621	2.383
Absorption coefficient (mm^{-1})		0.555	1.558	1.171	6.374	5.037
F(000)		940	798	494	302	708
Crystal size (mm)		0.39 x 0.17 x 0.11	0.21 x 0.14 x 0.06	0.55 x 0.16 x 0.02	0.40 x 0.11 x 0.05	0.31 x 0.07 x 0.03
Theta range for data collection (°)		1.77 to 22.00	2.08 to 26.41	2.39 to 26.52	2.72 to 26.40	2.31 to 26.47
Reflections collected		22286	17035	12431	5167	12966
Independent reflections [R(int)]		5978 [0.0677]	5337 [0.0305]	3936 [0.0388]	1647 [0.0118]	2116 [0.0600]
Observed reflections [$I>2\sigma(I)$]		3727	4111	2993	1586	1561
Data / restraints / parameters		5978 / 96 / 690	5337 / 0 / 407	3936 / 0 / 290	1647 / 0 / 111	2116 / 0 / 153
Goodness-of-fit on F^2		0.940	1.022	1.017	1.080	0.974
R_1 [I>2sigma(I)]		0.0460	0.0379	0.0385	0.0206	0.0330
Wr_2 (all data)		0.1306	0.1133	0.1057	0.0546	0.0749

Table C4 – Crystal data and X-ray experimental details for **3.15**, **3.27**, **3.29**, **3.31** and **3.32**.

Compound		**3.15**	**3.27**	**3.29**	**3.31**	**3.32**
Empirical formula		$C_{16}H_{14}AgN_5O_5$	$C_{18}H_{18}N_3O_6Ag$	$C_{36}H_{32}N_6O_{10}Cu$	$C_{47}H_{46}N_2O_6P_2Cu$	$C_{36}H_{32}N_6O_{10}Cd$
Formula weight		464.19	480.22	772.22	860.34	821.08
Temperature (K)		168(2)	168(2)	168(2)	168(2)	168(2)
Crystal system		Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group		C2/c	P-1	$P2_1/n$	P-1	$P2_1/n$
Unit cell dimensions:	a (Å)	20.790(18)	5.465(5)	8.437(7)	9.391(2)	8.351(7)
	b (Å)	6.409(6)	6.931(6)	16.901(17)	12.588(3)	16.900(15)
	c (Å)	13.530(12)	23.47(2)	11.904(10)	19.413(5)	12.515(11)
	α (°)	90	84.090(10)	90	82.479(3)	90
	β (°)	105.544(12)	85.770(11)	103.93(3)	78.511(3)	104.052(11)
	γ (°)	90	89.558(13)	90	74.685(3)	90
Volume($Å^3$)		1737(3)	882.0(13)	1648(3)	2161.5(9)	1713(3)
Z		4	2	2	2	2
Density (calculated) (Mg/m^3)		1.775	1.808	1.557	1.322	1.591
Absorption coefficient (mm^{-1})		1.201	1.186	0.735	0.630	0.707
F(000)		928	484	798	898	836
Crystal size (mm)		0.40 x 0.31 x 0.09	0.55 x 0.46 x 0.16	0.44 x 0.15 x 0.02	0.69 x 0.64 x 0.45	0.24 x 0.20 x 0.14
Theta range for data collection (°)		2.03 to 26.33	2.62 to 26.40	2.14 to 26.41	1.92 to 26.39	2.07 to 26.43
Reflections collected		10438	10508	21246	25900	21379
Independent reflections [R(int)]		1751 [0.0277]	3469 [0.0257]	3370 [0.0798]	8540 [0.0216]	3459 [0.0632]
Observed reflections [$I>2\sigma(I)$]		1583	3207	1746	7595	2439
Data / restraints / parameters		1751 / 0 / 129	3469 / 0 / 259	3370 / 0 / 241	8540 / 0 / 527	3459 / 0 / 241
Goodness-of-fit on F^2		1.075	1.191	0.809	1.029	0.934
R_1 [I>2sigma(I)]		0.0372	0.0359	0.0347	0.0330	0.0311
wR_2 (all data)		0.1060	0.0930	0.0633	0.0928	0.0677

Table C5 – Crystal data and X-ray experimental details for **3.33**, **3.36**, **3.38**, **3.43** and **3.44**.

Compound		**3.33**	**3.36**	**3.38**	**3.43**	**3.44**
Empirical formula		$C_{18}H_{16}N_2O_2ZnBr_2$	$C_{20}H_{20}N_4O_8CuCl_4$	$C_{36}H_{34}Cd_{1.5}N_7O_{14}$	$C_{18}H_{16}N_3O_5Ag$	$C_{18}H_{16}Cl_2N_2O_2Cu$
Formula weight		517.52	649.74	957.30	462.21	426.77
Temperature (K)		168(2)	293(2)	168(2)	168(2)	168(2)
Crystal system		Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group		$P2_1/n$	P-1	P-1	P-1	C2/c
Unit cell dimensions:	a (Å)	9.794(3)	9.676(5)	10.767(11)	14.141(5)	10.531(3)
	b (Å)	14.896(5)	11.204(5)	13.142(14)	15.131(5)	19.541(6)
	c (Å)	13.101(4)	12.645(5)	15.561(16)	16.909(6)	8.801(3)
	α (°)	90	84.055(5)	102.889(14)	90.117(4)	90
	β (°)	101.564(5)	86.134(5)	99.098(15)	110.099(5)	100.951(4)
	γ (°)	90	77.863(5)	92.993(15)	94.830(5)	90
Volume(Å^3)		1872.5(10)	1331.5(11)	2110(4)	3384(2)	1778.2(9)
Z		4	2	2	8	4
Density (calculated) (Mg/m^3)		1.836	1.621	1.506	1.815	1.594
Absorption coefficient (mm^{-1})		5.593	1.273	0.834	1.229	1.543
F(000)		1016	658	966	1856	868
Crystal size (mm)		0.41 x 0.22 x 0.11	0.29 x 0.24 x 0.12	0.34 x 0.24 x 0.11	0.31 x 0.25 x 0.05	0.61 x 0.59 x 0.32
Theta range for data collection (°)		2.09 to 26.36	2.16 to 26.43	1.84 to 26.38	1.89 to 26.51	2.08 to 26.32
Reflections collected		11230	16697	26411	43052	10645
Independent reflections [R(int)]		3726 [0.0263]	5283 [0.0278]	8319 [0.1010]	13524 [0.0361]	1756 [0.0263]
Observed reflections [I>2σ(I)]		2435	4179	4598	7851	1627
Data / restraints / parameters		3726 / 0 / 226	5283 / 0 / 347	8319 / 0 / 544	13524 / 0 / 973	1756 / 0 / 114
Goodness-of-fit on F^2		0.840	1.031	1.088	0.823	1.114
R_1 [I>2sigma(I)]		0.0299	0.0419	0.0692,	0.0272	0.0554
wR_2 (all data)		0.0607	0.1142	0.2038	0.0544	0.1583

Table C6 – Crystal data and X-ray experimental details for **3.47**, **3.49**, **3.50**, **3.51** **3.54**

Compound		**3.47**	**3.49**	**3.50**	**3.51**	**3.54**
Empirical formula		$C_{20}H_{19}AgN_4O_5$	$C_{18}H_{22}N_3O_8Cd_{0.50}$	$C_{18}H_{16}N_2O_2ZnBr_2$	$C_{18}H_{16}N_3O_5Ag$	$C_{20}H_{22}N_2O_3Cl_2ZnBr_2$
Formula weight		503.26	464.59	517.52	462.21	634.49
Temperature (K)		168(2)	168(2)	168(2)	168(2)	168(2)
Crystal system		Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group		$P2_1/c$	$C222_1$	P-1	C2/c	$P2_1/n$
Unit cell dimensions:	a (Å)	11.827(5)	8.575(4)	9.295(3)	11.560(4)	11.001(12)
	b (Å)	22.938(9)	20.603(9)	9.854(3)	17.727(6)	10.548(11)
	c (Å)	8.104(3)	22.817(10)	11.309(4)	8.641(3)	21.21(2)
	α (°)	90	90	101.703(5)	90	90
	β (°)	108.133(5)	90	93.901(4)	98.569(5)	95.60(5)
	γ (°)	90	90	112.883(4)	90	90
Volume(Å^3)		2089.5(14)	4031(3)	922.1(5)	1751.0(11)	2450(4)
Z		4	8	2	4	4
Density (calculated) (Mg/m^3)		1.600	1.531	1.864	1.753	1.720
Absorption coefficient (mm^{-1})		1.004	0.621	5.679	1.187	4.506
F(000)		1016	1912	508	928	1256
Crystal size (mm)		0.59 x 0.57 x 0.07	0.45 x 0.41 x 0.02	0.25 x 0.21 x 0.05	0.34 x 0.24 x 0.17	0.43 x 0.17 x 0.12
Theta range for data collection (°)		2.02 to 26.59	2.17 to 26.43	2.32 to 26.52	2.30 to 26.36	1.93 to 22.50
Reflections collected		25798	25808	11652	6142	8937
Independent reflections [R(int)]		4289 [0.0434]	4122 [0.0503]	3687 [0.0247]	1778 [0.0212]	3128 [0.0736]
Observed reflections [I>2σ(I)]		3524	3571	2961	1468	2238
Data / restraints / parameters		4289 / 0 / 272	4122 / 0 / 287	3687 / 0 / 226	1778 / 0 / 125	3128 / 0 / 265
Goodness-of-fit on F^2		1.094	0.955	0.963	1.121	1.101
R_1 [I>2sigma(I)]		0.0377	0.0269	0.0296	0.0445	0.0960
wR_2 (all data)		0.0886	0.0500	0.0730	0.0936	0.2403

Table C7 – Crystal data and X-ray experimental details for **3.58**, **3.61**, **3.62**, **3.68** and **3.73**.

Compound		**3.58**	**3.61**	**3.62**	**3.68**	**3.73**
Empirical formula		$C_{18}H_{16}N_3O_5Ag$	$C_{18}H_{16}N_2O_3ZnBr_2$	$C_{18}H_{16}N_3O_5Ag$	$C_{18}H_{17}Cd_{0.5}N_3O_{5.5}$	$C_{24}H_{21}Ag_2N_5O_9$
Formula weight		462.21	533.52	462.21	419.55	739.20
Temperature (K)		168(2)	168(2)	273(2)	293(2)	168(2)
Crystal system		Monoclinic	Monoclinic	Monoclinic	Othorhombic	Triclinic
Space group		$P2_1/n$	$P2_1/c$	C2/c	Pnma	P-1
Unit cell dimensions:	a (Å)	14.688(4)	8.851(4)	15.637(18)	28.266(11)	8.297(6)
	b (Å)	7.976(5)	16.429(8)	9.068(11)	17.411(7)	10.520(8)
	c (Å)	15.663(2)	14.573(7)	28.26(4)	6.971(3)	14.946(11)
	α (°)	90	90	90	90	78.690(10)
	β (°)	109.830(4)	94.612(7)	94.48(4)	90	75.663(9)
	γ (°)	90	90	90	90	84.997(10)
Volume(Å^3)		1726.1(11)	2112.2(18)	3994(8)	3431(2)	1238.3(16)
Z		4	4	8	8	2
Density (calculated) (Mg/m^3)		1.779	1.678	1.537	1.625	1.982
Absorption coefficient (mm^{-1})		1.205	4.964	1.041	0.710	1.647
F(000)		928	1048	1856	1712	732
Crystal size (mm)		0.56 x 0.34 x 0.06	0.24 x 0.23 x 0.14	0.25 x 0.14 x 0.05	0.34 x 0.13 x 0.08	0.29 x 0.25 x 0.19
Theta range for data collection (°)		2.34 to 26.39	2.48 to 26.49	2.60 to 26.36	1.86 to 26.39	1.98 to 26.43
Reflections collected		9049	21746	2824	41836	15419
Independent reflections [R(int)]		3483 [0.0294]	4332 [0.1141]	2663 [0.0223]	3631 [0.0584]	4963 [0.0204]
Observed reflections [I>2σ(I)]		2903	2201	1494	3396	4441
Data / restraints / parameters		3483 / 0 / 263	4332 / 6 / 235	2663 / 0 / 277	3631 / 0 / 262	4963 / 0 / 361
Goodness-of-fit on F^2		1.193	0.938	1.365	1.328	1.157
R_1 [I>2sigma(I)]		0.0498	0.0487	0.1307	0.0989	0.0297
wR_2 (all data)		0.0854	0.1127	0.2869	0.1835	0.0738

Table C8 – Crystal data and X-ray experimental details for **3.74**, **3.76**, **3.77**, **3.83** and **4.3**.

Compound		**3.74**	**3.76**	**3.77**	**3.83**	**4.3**
Empirical formula		$C_{24}H_{21}Cl_2CuN_3O_3$	$C_{24}H_{21}N_3O_3ZnBr_2$	$C_{28}H_{27}Ag_{1.5}B_{1.5}F_6N_5O_3$	$C_{24}H_{21}CdN_5O_9$	$C_{12}H_{16}AgN_3O_3$
Formula weight		533.88	624.63	773.57	635.86	358.15
Temperature (K)		168(2)	168(2)	168(2)	168(2)	168(2)
Crystal system		Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group		C2/m	P-1	P-1	C2/c	C2
Unit cell dimensions:	a (Å)	24.055(14)	7.737(3)	11.151(3)	27.021(5)	23.853(14)
	b (Å)	17.695(10)	12.189(5)	11.553(3)	16.815(5)	7.279(4)
	c (Å)	8.012(5)	14.145(6)	12.764(3)	17.961(5)	7.284(4)
	α (°)	90	103.938(5)	75.628(4)	90	90
	β (°)	108.696(7)	100.083(5)	82.693(3)	125.498(5)	94.479(9)
	γ (°)	90	104.705(5)	68.782(3)	90	90
Volume(Å^3)		3230(3)	1212.0(9)	1483.5(7)	6644(3)	1260.8(12)
Z		4	2	2	8	4
Density (calculated) (Mg/m^3)		1.098	1.712	1.732	1.271	1.887
Absorption coefficient (mm^{-1})		0.865	4.341	1.078	0.706	1.607
F(000)		1092	620	772	2560	720
Crystal size (mm)		0.55 x 0.34 x 0.12	0.51 x 0.17 x 0.09	0.61 x 0.52 x 0.24	0.27 x 0.12 x 0.09	0.34 x 0.11 x 0.10
Theta range for data collection (°)		2.30 to 26.38	2.70 to 26.40	2.23 to 26.39	2.40 to 26.38	2.80 to 26.41
Reflections collected		20302	15431	17890	23792	4048
Independent reflections [R(int)]		3373 [0.1024]	4824 [0.0429]	5834 [0.0149]	6646 [0.0977]	1615 [0.0318]
Observed reflections [I>2σ(I)]		1806	2925	5412	3009	1348
Data / restraints / parameters		3373 / 0 / 210	4824 / 0 / 363	5834 / 0 / 428	6646 / 0 / 378	1615 / 1 / 190
Goodness-of-fit on F^2		1.045	0.881	1.085	1.250	1.050
R_1 [I>2sigma(I)]		0.0850	0.0339	0.0339	0.1079	0.0326
wR_2 (all data)		0.3142	0.0694	0.0842	0.2588	0.0800

Table C9 – Crystal data and X-ray experimental details for **4.4**, **4.5**, **4.6**, **4.7**nd **4.8**.

Compound		**4.4**	**4.5**	**4.6**	**4.7**	**4.8**
Empirical formula		$C_{12}H_{16}Cu_{0.5}N_3O_4$	$C_{12}H_{16}CuIN_2$	$C_{24}H_{32}N_4Zn\ Br_2$	$C_{20}H_{28}N_2$	$C_{20}H_{28}N_2$
Formula weight		298.05	378.71	601.73	296.44	296.44
Temperature (K)		168(2)	168(2)	168(2)	163(2)	168(2)
Crystal system		Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Space group		$C222_1$	C2	$P2_1$	$P2_12_12$	$P4_12_12$
Unit cell dimensions:	a (Å)	7.494(6)	27.931(8)	10.559(4)	10.752(6)	10.816(4)
	b (Å)	30.58(3)	12.439(4)	19.801(8)	11.359(6)	10.816(4)
	c (Å)	12.065(11)	15.743(5)	12.833(5)	7.382(4)	14.978(10)
	α (°)	90	90	90	90	90
	β (°)	90	100.842(4)	103.811(5)	90	90
	γ (°)	90	90	90	90	90
Volume(Å^3)		2765(4)	5372(3)	2605.5(17)	901.6(8)	1752.3(14)
Z		8	16	4	2	4
Density (calculated) (Mg/m^3)		1.432	1.873	1.534	1.092	1.124
Absorption coefficient (mm^{-1})		0.847	3.901	4.027	0.064	0.065
F(000)		1244	2944	1216	324	648
Crystal size (mm)		0.45 x 0.14 x 0.01	0.58 x 0.46 x 0.04	0.71 x 0.56 x 0.11	0.56 x 0.07 x 0.07	0.79 x 0.65 x 0.49
Theta range for data collection (°)		2.15 to 26.37	2.14 to 26.39	1.93 to 26.45	2.61 to 26.39	2.32 to 26.32
Reflections collected		17093	33868	33660	10913	21384
Independent reflections [R(int)]		2800 [0.2514]	9962 [0.0311]	10518 [0.0493]	1835 [0.0495]	1779 [0.0532]
Observed reflections [I>2σ(I)]		1551	8940	9428	1485	1674
Data / restraints / parameters		2800 / 0 / 187	9962 / 1 / 577	10518 / 1 / 559	1835 / 0 / 100	1779 / 0 / 101
Goodness-of-fit on F^2		1.101	1.170	1.032	1.059	1.080
R_1 [I>2sigma(I)]		0.1248	0.0510	0.0922	0.0441	0.0377
wR_2 (all data)		0.2774	0.1343	0.2300	0.1154	0.1083

Table C10 – Crystal data and X-ray experimental details for **4.9**, **4.10**, **4.11** and **4.14**.

Compound		**4.9**	**4.10**	**4.11**	**4.14**
Empirical formula		$C_{20.75}H_{32}AgN_3O_{4.25}$	$C_{60}H_{84}Cu_4I_4N_6$	$C_{20}H_{28}AgN_3O4$	$C_{26}H_{30}Ag_2N_6O_8$
Formula weight		499.36	1651.09	482.32	770.30
Temperature (K)		163(2)	163(2)	168(2)	168(2)
Crystal system		Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group		$P2_12_12$	C2	$P2_12_12_1$	$P2_12_12$
Unit cell dimensions:	a (Å)	13.614(5)	23.808(9)	13.721(4)	7.368(3)
	b (Å)	28.871(10)	14.984(6)	14.368(4)	28.931(10)
	c (Å)	11.523(5)	18.715(7)	22.876(6)	c7.214(2)
	α (°)	90	90	90	90
	β (°)	90	94.265(5)	90	90
	γ (°)	90	90	90	90
Volume($Å^3$)		4529(3)	6658(5)	4510(2)	1537.8(9)
Z		8	4	8	2
Density (calculated) (Mg/m^3)		1.465	1.647	1.421	1.664
Absorption coefficient (mm^{-1})		0.921	3.154	0.922	1.329
F(000)		2068	3256	1984	772
Crystal size (mm)		0.40 x 0.12 x 0.04	0.70 x 0.31 x 0.21	0.46 x 0.12 x 0.10	0.47 x 0.11 x 0.02
Theta range for data collection (°)		2.06 to 26.38	1.96 to 26.43	1.67 to 26.45	2.82 to 26.39
Reflections collected		59156	37544	58511	18602
Independent reflections [R(int)]		9250 [0.0775]	13247 [0.0343]	9154 [0.0494]	3069 [0.0797]
Observed reflections [I>2σ(I)]		6208	12549	6966	2571
Data / restraints / parameters		9250 / 24 / 552	13247 / 1 / 714	9154 / 2 / 547	3069 / 0 / 207
Goodness-of-fit on F^2		0.890	1.040	0.999	1.058
R_1 [I>2sigma(I)]		0.0360	0.0414	0.0421	0.0555
wR_2 (all data)		0.0771	0.1057	0.1199	0.1560

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